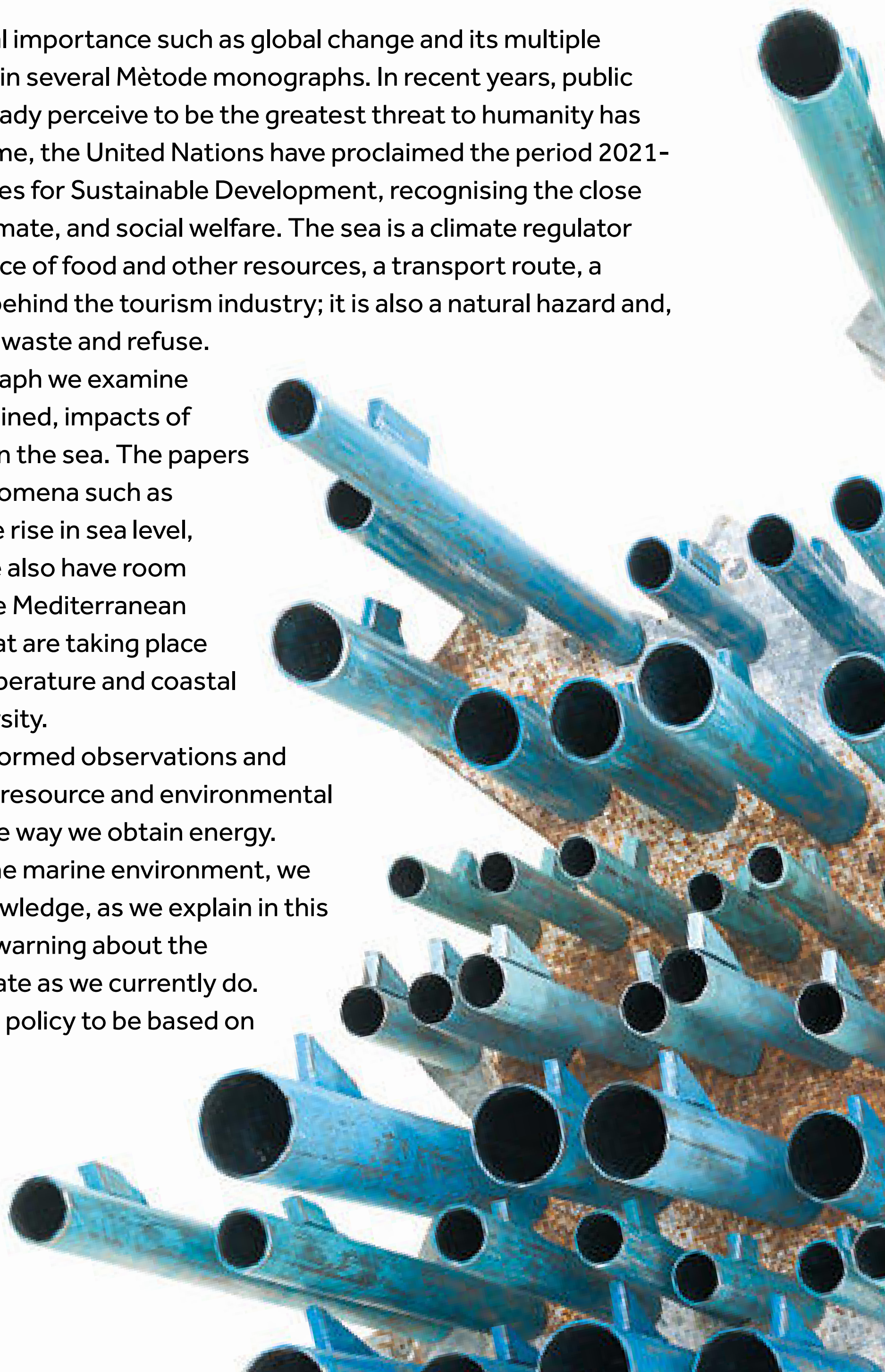
OCEANS
THE IMPACT OF GLOBAL CHANGE OF THE SEA

Monograph coordinated by Carles Pedrós-Alió, Josep M. Gasol and Rafel Simó

A phenomenon of exceptional importance such as global change and its multiple effects has been discussed in several Mètode monographs. In recent years, public concern about what we already perceive to be the greatest threat to humanity has not stopped growing; at the same time, the United Nations have proclaimed the period 2021-2030 as the Decade of Ocean Sciences for Sustainable Development, recognising the close relationship between the oceans, climate, and social welfare. The sea is a climate regulator and a reservoir of biodiversity, a source of food and other resources, a transport route, a cultural asset, and the driving force behind the tourism industry; it is also a natural hazard and, unfortunately, a dumping ground for waste and refuse.

Consequently, in this new monograph we examine some of the main, but as yet unexplained, impacts of climate and environmental change on the sea. The papers we present here analyse global phenomena such as acidification, deoxygenation, and the rise in sea level, as well as the impact of pollution. We also have room for more local studies, which take the Mediterranean Sea as an example of phenomena that are taking place everywhere: the increase in sea temperature and coastal algae growth and the loss of biodiversity.

Scientific knowledge, based on informed observations and interpretations, would have to guide resource and environmental management decisions, including the way we obtain energy. As researchers who work studying the marine environment, we generate much of the necessary knowledge, as we explain in this monograph, while at the same time warning about the consequences of continuing to operate as we currently do. Regarding political action, we expect policy to be based on this knowledge.



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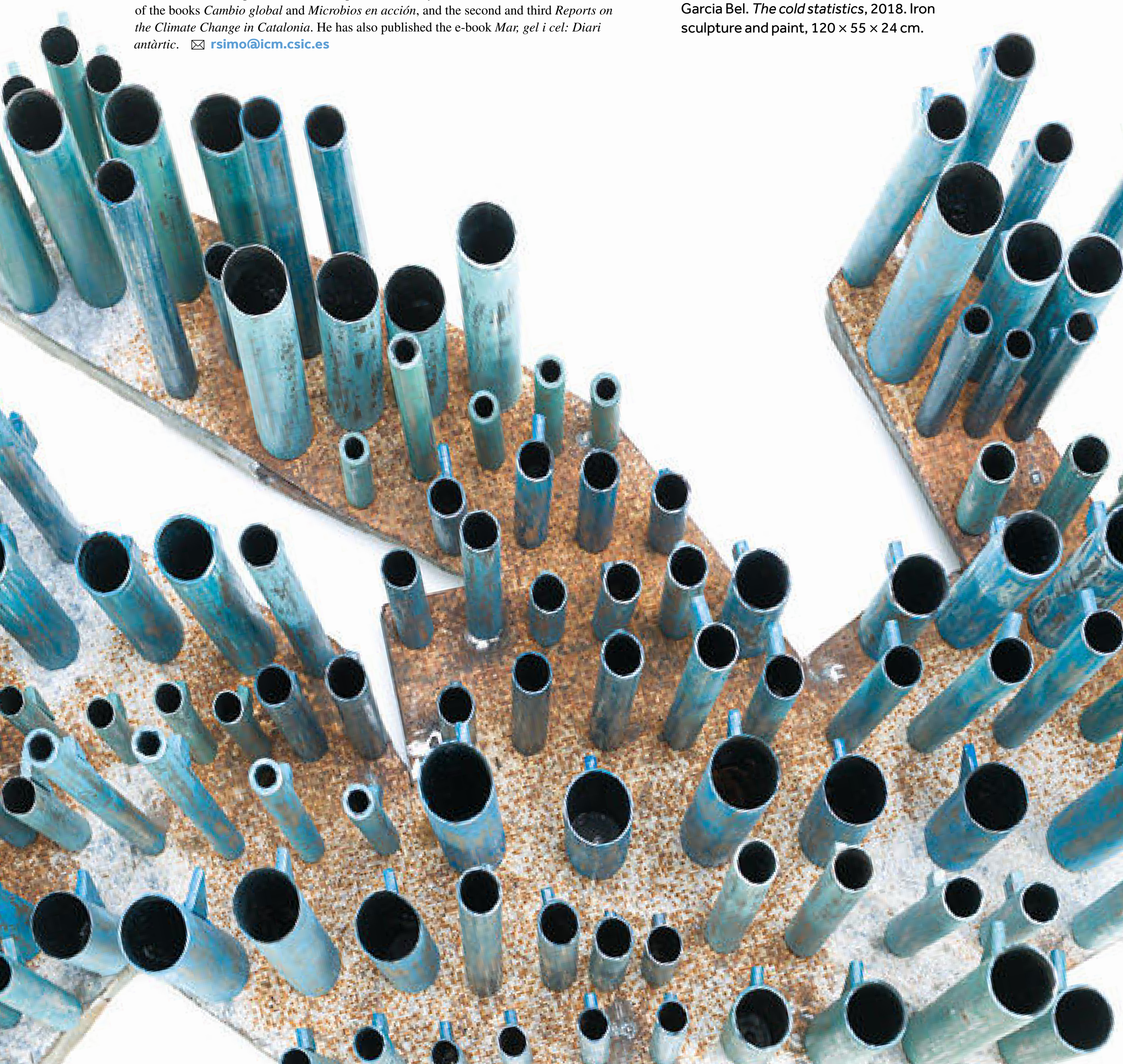
The work of the artist Garcia Bel (Tortosa, Spain, 1969) accompanies this issue devoted to the impact of the global change in the oceans. Everything he creates with lives a double life: one for the useful life of each material, and the one he gives them after they become waste. The artworks in the following pages are part of the series «From the sea». The collection is brimming with meaning, with nature rebelling against human dominance.



Garcia Bel. *The cold statistics*, 2018. Iron sculpture and paint, 120 × 55 × 24 cm.

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BEYOND GLOBAL WARMING

Stressed oceans, globe-wide in the Anthropocene

CARLES PELEJERO AND EVA CALVO

The footprint of human activities on the planet is so profound that many scientists are already suggesting that we have entered a new geological era, the Anthropocene. From among these activities, those that are accompanied by large emissions of carbon dioxide (CO_2) affect our entire planet and, especially, the oceans. Besides becoming warmer, the oceans are also growing progressively more acidic and less oxygenated. In this article we discuss the extent of these global stresses on the oceans after contextualising the disproportionate anthropogenic increase in CO_2 and examining how it is distributed. We conclude with a discussion of mitigation possibilities that use the oceans themselves, stressing the urgent need to tackle the problem, especially during this present decade.

Keywords: Anthropocene, warming, acidification, deoxygenation, global change.

THE DISPROPORTIONATE INCREASE IN ATMOSPHERIC CO_2

One of the most graphic and palpable ways to help understand the magnitude of the problem of anthropogenic CO_2 emissions is to compare the atmospheric concentrations of this greenhouse gas over recent decades with those of the past. We have had access to modern instrumental data since Charles David Keeling first began making measurements at an elevation of 3,400 m at Mauna Loa, Hawaii; now over 60 years ago, he initiated what is now known as the Keeling curve. His first analysis, in March 1958, measured 313 ppmv (parts per million by volume). Since then, the CO_2 concentrations at this summit – which was chosen so that an average atmospheric value would be obtained without being influenced by nearby industrial areas or large masses of vegetation – have increased continuously and progressively (following small annual cycles) and, in May 2013, they crossed the 400 ppm barrier. The 2019 average was 411 ppm, and in recent years atmospheric CO_2 has been increasing by between 2 to 3 ppm per year.

«The CO_2 absorbed by the oceans affects a number of chemical equilibriums and results in gradual ocean acidification»

For periods preceding the Keeling curve – earlier than 1958 – we have valuable evidence obtained from the ice accumulated over hundreds of thousands of years in Antarctica (Alley, 2014). As this ice compacts, air is trapped within it in the form of small bubbles, which preserve an extraordinary record of the composition of the atmosphere in the past. In some areas of Antarctica, we can find accumulations of more than three kilometres of ice. Through the study of these ice cores at the beginning of the 1980s, it was discovered that, in the last ice age, now approximately 20,000 years ago, the concentration of CO_2 in the air had been significantly lower than it is today (Delmas et al., 1980). After almost thirty years studying new ice cores, a continuous record of atmospheric CO_2 was obtained for the last 800,000 years, including a series of glacial/interglacial cycles (Lüthi et al., 2008). Recently, it became possible to determine CO_2 concentrations through the analysis of Antarctic ice for earlier, periods reaching back up to two million years, although we still do not yet have a continuous record covering such a long period (Yan et al., 2019).

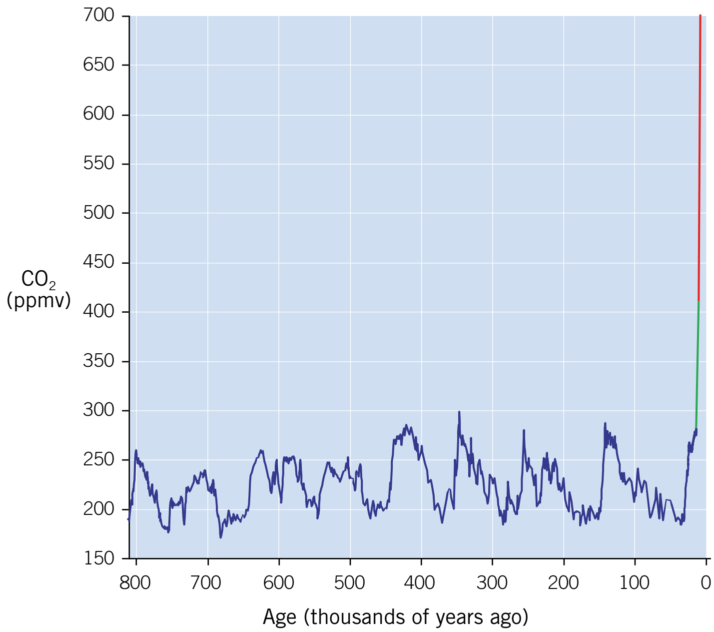


Figure 1. CO_2 concentration in the atmosphere in parts per million by volume (ppmv) for the last 800,000 years and up to the pre-industrial era (data measured in Antarctic ice cores are shown in blue; data from Lüthi et al. [2008]), in the last few centuries and up to the present (shown in green, as measured in ice cores and instruments; data from *The Keeling Curve* project, Scripps Institution of Oceanography, University of San Diego, California), and in future projections up to the end of the twenty-first century, according to intermediate emissions scenarios (shown in red).

SOURCE: Created by the authors from referenced sources

As can be seen in Figure 1, the continuous record of atmospheric CO_2 for the last 800,000 years shows values ranging from 180 ppm during the cold glacial periods to 280 ppm during the warm interglacial periods. In this context, the current values – already above 410 ppm – have clearly fallen outside the range of natural atmospheric CO_2 variability for, at least, the last 800,000 years. Depending on future socioeconomic models, energy policies and population growth, the concentration of CO_2 in the atmosphere will take different trajectories, which could exceed 1,000 ppm by the end of the century according to the most pessimistic scenarios, or reach values below 500 ppm in the most optimistic ones (Fuss et al., 2014).

HOW IS THIS CO_2 DISTRIBUTED?

Fundamentally, the CO_2 that humans release into the atmosphere is distributed into three major compartments: atmosphere, continents, and oceans (Figure 2). During the 2009–2018 period, it was estimated that 44 % of CO_2 emissions went into the atmosphere, 29 % went into the continents (fixed by plants), and 23 % was absorbed by the seas and oceans, with the remaining 4 % representing the current mismatch between the calculation of global emissions and sinks (Friedlingstein et al., 2019). These calculations are independent and, because of their inherent uncertainties, emissions and sinks often do not match perfectly. A positive mismatch, as in this case, either means that emissions are being overestimated, or that sink estimates are lower than the actual values. We should be grateful, therefore, that not all the CO_2 that humans release by burning of fossil fuels remains in the atmosphere and, most importantly, that it can be absorbed by plants and ocean waters. Were it not so, the concentration of CO_2 in the atmosphere would be significantly higher, thereby aggravating the greenhouse effect and global warming. However, as we will discuss below, the CO_2 absorbed by the oceans affects a number of chemical balances and results in gradual ocean acidification, which conditions the development of many marine organisms.

GLOBAL STRESSES RELATED TO THE INCREASE IN CO_2

Today, oceans and marine ecosystems are suffering from multiple stresses related to human activities, with impacts manifesting themselves both locally and globally. Some examples of these pressures include overfishing, pollution, destructive fishing techniques, eutrophication (increased nutrient availability), habitat destruction, species invasions, and maritime traffic, among others. In addition to these stresses, there are three more closely related to CO_2 emissions and climate change, and these generally manifest themselves globally in all the seas and oceans: warming, acidification, and deoxygenation (Gruber, 2011).

Warmer oceans

Without a doubt, the reports by the Intergovernmental Panel on Climate Change (IPCC) are becoming increasingly clear and conclusive – the enormous increase in atmospheric CO_2 is causing global warming on our planet. It is estimated that, since the beginning of industrialisation, the Earth's global surface temperature has already increased by about 1 °C. Regarding the oceans, much of the excess heat experienced by the Earth due to the greenhouse effect (around 90 %) is retained in its waters. Surface water has warmed, on average, by about 0.6–0.8 °C from pre-industrial times to 2010. Depending on future emissions scenarios, sea surface temperatures could

Figure 2. Annual CO_2 emissions (average for the period 2009–2018) derived from the burning of fossil fuels and deforestation, and the three compartments that act as CO_2 sinks: the atmosphere, ground vegetation, and oceans.

SOURCE: Adapted from Global Carbon Project (2019)

rise by an average of 0.7 °C to 2.6 °C more by the end of the twenty-first century, according to the most optimistic and pessimistic scenarios, respectively, compiled in a recent IPCC Special Report on the Ocean and Cryosphere (IPCC, 2019). To a lesser extent – but already measurable instrumentally – deep oceanic waters are also getting warmer, even below 4,000 m, especially in the Southern Ocean.

Such warming is having a major impact on ecosystems such as tropical coral reefs and Mediterranean coralligenous communities, marine forests such as the *Posidonia oceanica* meadows or kelp forests, and phytoplankton species, among others. For example, the increasingly frequent ocean heat waves cause coral bleaching episodes and mass mortality among sessile species. The 2016 marine heat wave on the Great Barrier Reef off the north-eastern coast of Australia, for instance, killed one-third of the shallowest corals (GBRMPA, 2017).

«Much of the excess heat experienced by the Earth due to the greenhouse effect is retained in oceanic waters»

More acidic oceans

In addition to the global warming of marine waters, another planetary problem also caused by the exorbitant increase in atmospheric CO_2 has been intensively studied for the last fifteen years or so. Because this greenhouse gas dissolves in seawater, it interferes with a series of chemical reactions – the equilibriums between carbonic acid and bicarbonate and carbonate ions – resulting in an increase in proton concentration, i.e., increased water acidity or corrosiveness. It is estimated that the pH of ocean surface water has decreased, on average, by about 0.1 units from pre-industrial times to 2010 (Pelejero et al., 2010). Indeed, over the past few decades, pH has been declining at speeds of between 0.017 and 0.027 units per decade and, depending on future emissions scenarios, the marine surface pH could fall by a further 0.04 to 0.29 units, on average, by the end of the twenty-first century, according to the most optimistic or pessimistic scenarios, respectively (IPCC, 2019; see Figure 3).

This change in water chemistry has many implications for marine organisms, especially those that build calcium carbonate structures, such as corals, bivalves, gastropods, crustaceans and coccolithophores. Under higher acidity conditions these organisms often find it more difficult to build their shells, structures, and skeletons, which are also more likely to deteriorate and dissolve. Acidification stress adds to global warming

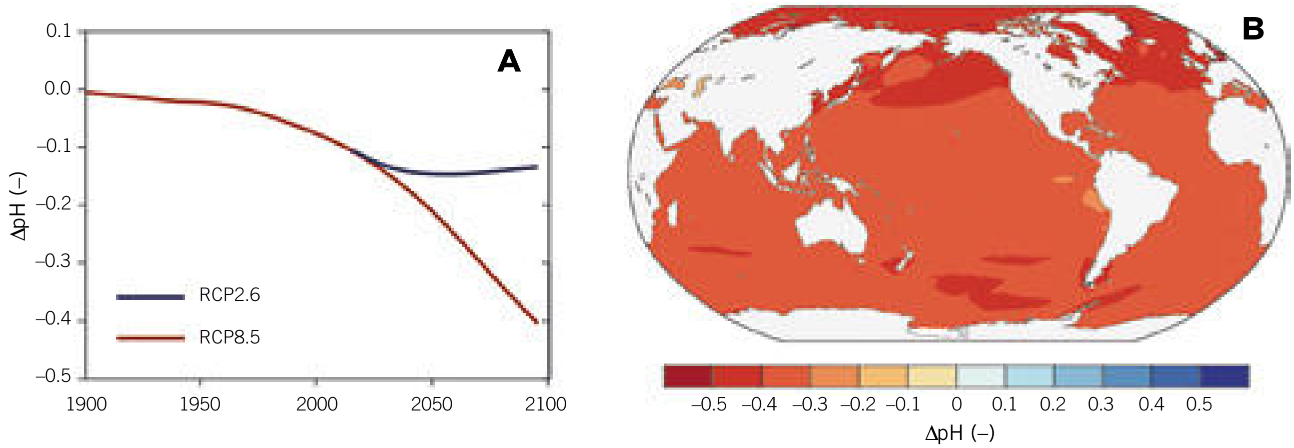


Figure 3. **A**) Simulation of past and future changes in global oceanic surface water pH according to optimistic (RCP2.6) and pessimistic (RCP8.5) scenarios. **B**) Changes in the surface pH of the oceans by the end of the twenty-first century in relation to the 1850–1900 period, according to a pessimistic scenario (RCP8.5). See Fuss et al. (2014) for more information on Representative Concentration Pathways (RCP) emission scenarios.

SOURCE: IPCC (2019, p. 470)

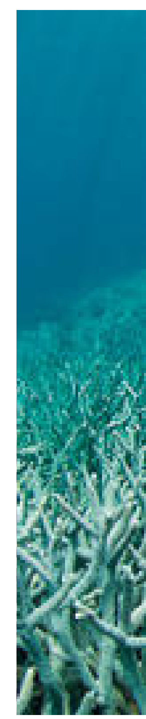
and often also interacts synergistically to further affect marine organisms. In the case of tropical corals, for example, which are already affected very significantly by global warming, when we add up the effect of acidification, which turns their structures more fragile and vulnerable, that means that they may have more difficulties to recover, for instance, after a bleaching event (Figure 4).

Less oxygenated oceans

More recently – in the last five to ten years – a third global stressor has also become the focus of a lot of attention from the marine scientific community: the progressive water deoxygenation. This phenomenon is also closely related to the increase in atmospheric CO_2 and climate change. In part, this phenomenon is caused by the warming of the oceans: the warmer the water, the less soluble the gases dissolved in it are. Under warmer conditions, oxygen has a greater tendency to escape from the water into the air. Unlike warming and acidification, which are more intense at the oceanic surface, in the open sea the problem of global deoxygenation is more pronounced in deeper depths, while the more superficial layers are usually highly oxygenated. The process also depends on the ocean basin. The Atlantic Ocean, for example, is better ventilated and is, therefore, better oxygenated than the Indian or Pacific Oceans, with the latter having the lowest levels of oxygen, particularly in its intermediate layers. Oxygen levels in the equatorial Pacific Ocean, at a depth of between 200 and 1,000 m, are particularly low.

«Some studies suggest that over the last five decades the oxygen content of the oceans has decreased by 2 %»

As for marine animals, only species adapted to living in such chemical conditions, like certain species of demersal fish or some cephalopods such as the giant squid can be found living in these oxygen-poor regions. The warming of the waters also results in greater stratification of the water column and less ventilation which, in turn, contributes to the progressive deoxygenation. In addition, warmer conditions boost the metabolism of marine organisms and, as a result, increases their demand for oxygen for respiration. In some coastal areas, the excessive production of organic matter due to eutrophication processes can also lead to the formation of localised areas with low levels of oxygen. Some studies suggest that, over the last five decades, the oxygen content of the oceans has decreased by 2 % (Schmidtko et al., 2017). Depending on future emissions scenarios, dissolved oxygen concentrations in the ocean water column could fall by a further 1.8 % to 3.5 % on average by the end of the twenty-first century, according to the most optimistic or pessimistic scenarios, respectively (IPCC, 2019; see Figure 5).



HOW TO TACKLE THE PROBLEM: INTERNATIONAL AGREEMENTS

At the 2015 United Nations Climate Change Conference in Paris, a major international agreement was reached to reduce CO_2 emissions, which entered into force at the end of 2016. This agreement required developed countries to commit to progressively reducing emissions with the aim of keeping the increase in average global temperature below 2 °C compared to pre-industrial values, taking into account that the increase now stands at 1 °C. However, the commitments adopted so far by the different countries still leave us far from the objective set out in Paris. Later, a special report (IPCC, 2018) warned that this 2 °C warming, despite being an ambitious objective, would still be insufficient to avoid triggering irreversible changes. Specifically in relation to the oceans, it will be vital to limit warming to 1.5 °C to reduce the risks posed to marine biodiversity, fishing, and marine ecosystems, as well as to their functions and the ecosystem services they provide to humans. Among the effects of climate change on the most at-risk ecosystems, this report highlighted the recent alarming decline in Arctic marine ice as well as the changes in the ecosystems associated with tropical coral reefs. The Paris agreement, therefore, is a good international starting point for addressing the root cause of all these global changes (and specially, the disproportionate anthropogenic release of CO_2) but ideally, it should be much more ambitious in terms of aiming to reduce emissions. In fact, as denounced in scientific reports and articles (see Höhne et al., 2020; United Nations Environment Programme, 2019), not much has been done in the last decade in terms of individual countries' policies to move in this direction.

The Ocean Agency / XL Catlin Seaview Survey

Figure 4. Acidification, caused by the dissolution of carbon dioxide in water, represents an additional stress on corals and other organisms that build calcium carbonate structures, because they are less able to regenerate after a bleaching process such as the one shown in the picture, taken in Australia's Great Barrier Reef.

«This change in water chemistry has many implications for marine organisms, especially those that build calcium carbonate structures»

POTENTIAL SOLUTIONS IN THE OCEANS THEMSELVES

Some of the solutions to help reduce the emissions of CO_2 and other greenhouse gases can, in fact, be found in the oceans themselves. For example, a recent report suggested a number of ocean-based fields of action that could be used to mitigate emissions (Hoegh-Guldberg, 2019). The oceans offer, for instance, great potential for renewable energy through the use of the energy stored in marine currents, tides, and waves, or with the construction of offshore wind farms. However, it must also be considered that many of these are still in the initial research or pilot phases and, therefore, will require a great deal more research and effort before their implementation. Emissions from maritime transport, which currently represent approximately 2–3 % of all anthropogenic CO_2 emissions, must also be reduced. This can be achieved by increasing energy efficiency, i.e., by reducing the energy required to move ships, or by replacing fossil fuels with other fuels that do not produce carbon emissions (e.g., hydrogen, ammonia, or some biofuels). As for oceanic carbon sequestration, the so-called marine forests, which include coastal ecosystems such as kelp forests, Posidonia meadows (Figure 6B), wetlands, or marshes, are very effective carbon sinks (collectively known as «blue carbon»), which can capture ten times more carbon per hectare than terrestrial ecosystems such as tropical forests (Mcleod et al., 2011). Thus, protecting these ecosystems, which are highly degraded by anthropogenic activities and global warming, will be key to reducing CO_2 because they play an important role in producing oxygen and protecting the coast from marine storms, cyclones, and tsunamis, and from the rise in sea levels resulting from climate change. Also related to marine organisms, macroalgae

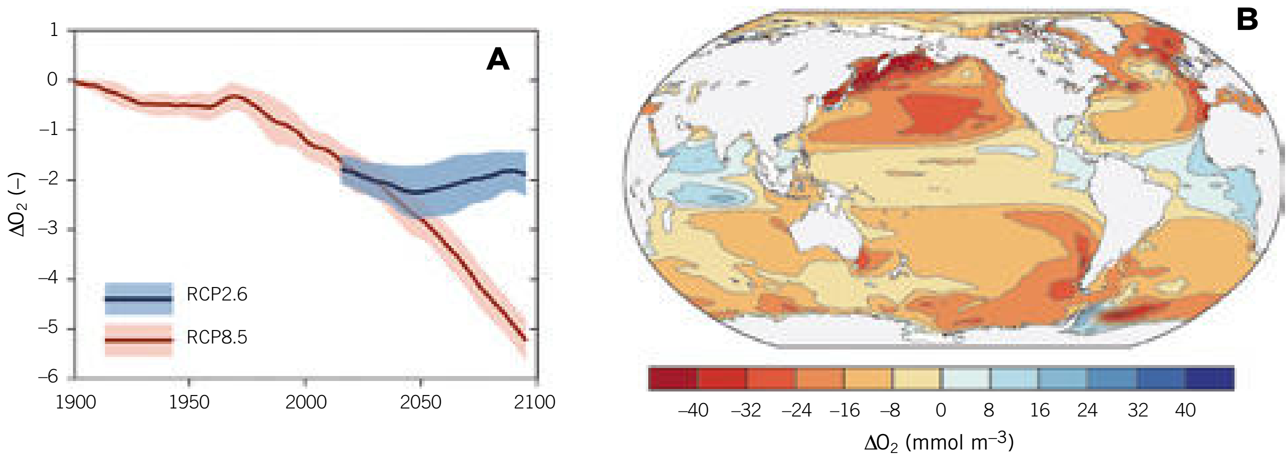


Figure 5. **A**) Simulation of past and future changes in the average dissolved oxygen concentration in the water column between 100 and 600 m depth, according to optimistic (RCP2.6) and pessimistic scenarios (RCP8.5). **B**) Spatial changes in the average dissolved oxygen concentration in the water column between 100 and 600 m depth by the end of the twenty-first century in relation to the 1850–1900, period according to a pessimistic scenario (RCP8.5). See Fuss et al. (2014) for more information on RCP emission scenarios.

SOURCE: IPCC (2019, p. 470)

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crops have a great potential as replacements for oil-derived compounds or even as a possible food supplement to reduce methane emissions from ruminant livestock (Machado et al., 2016).

URGENT ACTION MUST BE TAKEN

This brand-new decade will be key in trying to reverse this problem or, at least, to minimise its effects as far as possible. As stated in the latest Emissions Gap Report from the UN Environment Programme (2019), we have very little room for manoeuvre; we cannot afford another decade without taking drastic action or it will be impossible to achieve the maximum warming target of 1.5 °C or even 2.0 °C (Höhne et al., 2020). We require urgent and concerted action by every country and all our industrial sectors. Current policies on energy efficiency must be extended and strengthened, transport and mobility with minimal CO_2 emissions must be promoted, and an ambitious transition towards renewable energies must be promoted, while also bearing in mind that the planet's resources are limited, not only regarding fossil fuels. We are the last generation capable of avoiding irreversible and catastrophic changes, and the first that is already beginning to suffer their effects. In addition, we should not lose sight of the fact that the problem of climate change and global change can only be solved by a major social transformation. We should all ask ourselves what kind of world we want to live in and leave to future generations. It is very important that we become aware of all these environmental problems, the effects they have at the planetary scale, and the magnitude of our footprint, which is very comparable to the geological processes of the past.

«We are the last generation capable of avoiding irreversible and catastrophic changes, and the first that is already beginning to suffer their effects»

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Figure 6. The oceans can play an important role agents in the mitigation and reduction of carbon dioxide emissions, either as potential generators of renewable energy or through carbon sequestration. **A**) An offshore wind farm in the United Kingdom. **B**) Offshore forests, such as the *Posidonia oceanica* meadows shown in the image, are effective carbon sinks.

«In order to reduce the release of CO_2 and other greenhouse gases by humans, some solutions can be found in the oceans themselves»

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SEA-LEVEL RISE

Which is the role of glaciers and polar ice sheets?

FRANCISCO JOSÉ NAVARRO

Sea-level has been rising at an accelerated rate during recent decades and is projected to continue increasing at an accelerated rate over the twenty-first century and beyond, mostly as a result of anthropogenic warming. A substantially raised sea level can have severe impacts on low-lying coastal areas, including coastal erosion and flooding of inhabited areas. Under continued climate warming, these impacts will be exacerbated by extreme meteorological events and extreme wave heights, posing severe risks to the human communities and coastal ecosystems. In this paper we review the recent advances on the contributions of glaciers and sheets to sea-level rise, in the light of the recently released IPCC Special Report on the Ocean and Cryosphere in a Changing Climate.

Keywords: Sea-level rise, glacier, ice-sheet, glacier mass balance, landed ice losses.

INTRODUCTION

Sea level has changed much in the past, in the order of tens of metres, in parallel with glacial cycles. Currently, it is increasing at a rate that has accelerated over recent decades, mostly as a result of anthropogenic warming. Low-lying coastal zones (<10 m above sea level) are at present inhabited by more than 680 million people, which is around 10 % of the world's population. An accelerated rising sea level, its associated flooding of coastal areas and the expected increase in the frequency of extreme sea-level events are therefore a matter of concern to human kind. We analyse in this paper the current and the projected rates of sea-level rise (SLR), with focus on the contribution to SLR by mass loss from glaciers and ice sheets. There is a huge number of recent studies on this matter. The publication of the IPCC Special Report on the Ocean and Cryosphere in a Changing Climate (SROCC) (IPCC, 2019), and its condensed Summary for Policymakers (SPM), which provide updated data and consensus estimates, will alleviate the need to refer to a large amount of bibliographical sources, as they can easily be found in that report. Consequently, we will refer frequently to it, indicating the particular bullets of the SPM and the sections of the full report where further detail and references can be found.

In what follows, we will often present data resulting from statistical estimates by indicating its median and its likely range (the central 66 % or, in other words, the range 17–83 % of its probability distribution), as shown in this example: SLR of 3.6 (3.1–4.1) mm/yr.

«The collapse of ice shelves increases the export of landed ice to the ocean, hence indirectly contributing to rising the sea level»

PRESENT SEA-LEVEL RISE RATE AND CURRENT CONTRIBUTIONS

The average rate of global mean sea level (GMSL) rise for the period 2006–2015 is of 3.6 (3.1–4.1) mm/yr, and shows a clear acceleration when compared with the average rate for the period 1901–1990, of 1.4 (0.8–2.0) mm/yr. As a consequence of this sustained increase, the mean sea level has risen a total of 0.16 (0.12–0.21) m over the period 1902–2015. This change stems from processes resulting from global warming, which has been estimated, for the period between 1850–1900 and 1986–2005, as 0.63 (0.57–0.69) °C. In particular, of the current SLR of 3.6 mm/yr, 1.8 (1.7–1.9) mm/

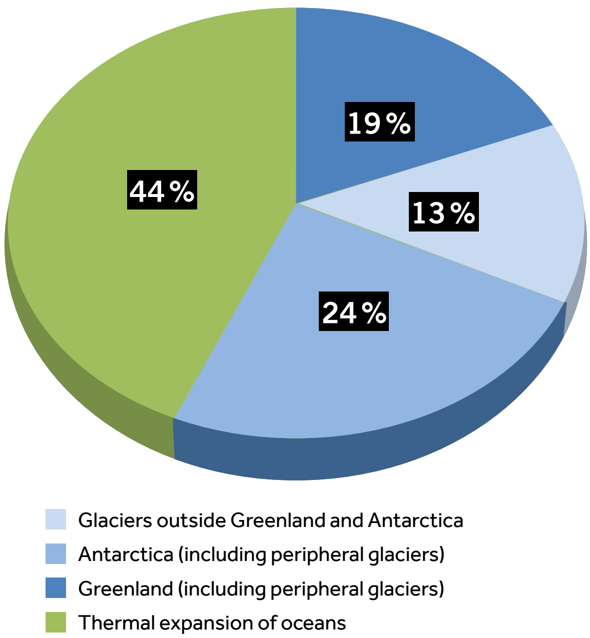


Figure 1. Share of observed positive contributions to global sea-level rise over the period 2006–2015. Land water storage changes do not appear because they were negative during this period (i.e., they contributed to lowering the sea level).

yr is attributed to wastage from glaciers and ice sheets[1], while 1.4 (1.1–1.7) mm/yr corresponds to thermal expansion of the ocean (Figure 1). The current estimated contribution from changes in the land water storage (at surface and underground) is negative, of −0.21 (−0.36–0.06) mm/yr., meaning that they contribute to lower the sea level. Taking into account the median values of these estimates, we see that 0.6 (out of 3.6, i.e., 17 %) mm/yr of observed SLR rise are unexplained, though within the uncertainty ranges (IPCC, 2019, SPM-A3.1, §4.2.2).

In this study we focus on the contributions from glaciers and ice sheets, i.e., from the landed ice masses. We note that sea-ice loss does not contribute to SLR, as the lower density of ice compared with water is the reason for its flotation, as stated by Archimedes' principle. Therefore, when sea ice melts to become water again it occupies less volume, exactly equal to that of its submerged part when it was ice. For the same reason, neither the melting of floating ice tongues or ice shelves contributes to SLR. However, the collapse of ice shelves contributes to the acceleration of the outlet glaciers feeding the ice shelves, thus increasing the export of landed ice to the ocean, and hence indirectly contributing to SLR (Rott et al., 2018).

From the 1.8 mm/yr contribution to SLR by mass loss from glaciers and ice sheets over 2006–2015, 0.61 ± 0.08 mm/yr correspond to glaciers outside of Greenland and Antarctica, 0.77 ± 0.03 mm/yr to Greenland (the ice sheet plus the glaciers on its periphery, disconnected from the main ice sheet) and 0.43 ± 0.05 mm/yr to Antarctica (the ice sheet plus its peripheral glaciers) (IPCC, 2019, SPM-A1.1, §3.3 & 4.2.2). Their corresponding shares of the sum of positive observed contributions are shown in Figure 1. We note the large contribution from glaciers as compared with ice sheets, taking into account its much lower total volume (the total volume of ice stored in glaciers, and in the Greenland and Antarctic ice sheets are roughly 0.5, 7 and 58 m sea-level equivalent, which means <1 %, ~11 % and >88 %, respectively; IPCC, 2019). This is due to the much shorter response time of glaciers to climate changes as compared with the ice sheets, due to their significantly smaller size.

«The Greenland Ice Sheet is currently losing mass at roughly twice the rate of the Antarctic Ice Sheet»

As we see, the Greenland Ice Sheet is currently losing mass at roughly twice the rate of the Antarctic Ice Sheet, though this could change in the coming centuries, as we will discuss later. The contribution from Greenland to SLR over 2012–2016 was quite similar to that over 2002–2011 but much larger than over 1992–2001, period at which the ice sheet mass was nearly in equilibrium. However, the contribution from Antarctica over 2012–2016 was nearly double than over 2002–2011, and four times larger than over 1992–2001. Regarding glaciers, their mass loss over 2006–2015 has been estimated as 9–10 % larger than over 1993–2015, and 33–37 % larger than over 1970–2015. The percent ranges depend on whether the estimates are based on observations or on models calibrated with observations, and whether they include or exclude the glaciers peripheral to the Greenland and Antarctic ice sheets (Bamber et al., 2018; Marzeion et al., 2017; Zemp et al., 2019).

PHYSICAL MECHANISMS OF MASS LOSS FROM GLACIERS TO THE OCEAN

There are various mechanisms of mass loss from glaciers and ice sheets (Figure 2), each predominant at a certain environment. Ice melting at surface

[1] Following common practice, we will distinguish between *glaciers* (encompassing both glaciers and ice caps) and *ice sheets*, which refers only to the large ice sheets of Greenland and Antarctica.

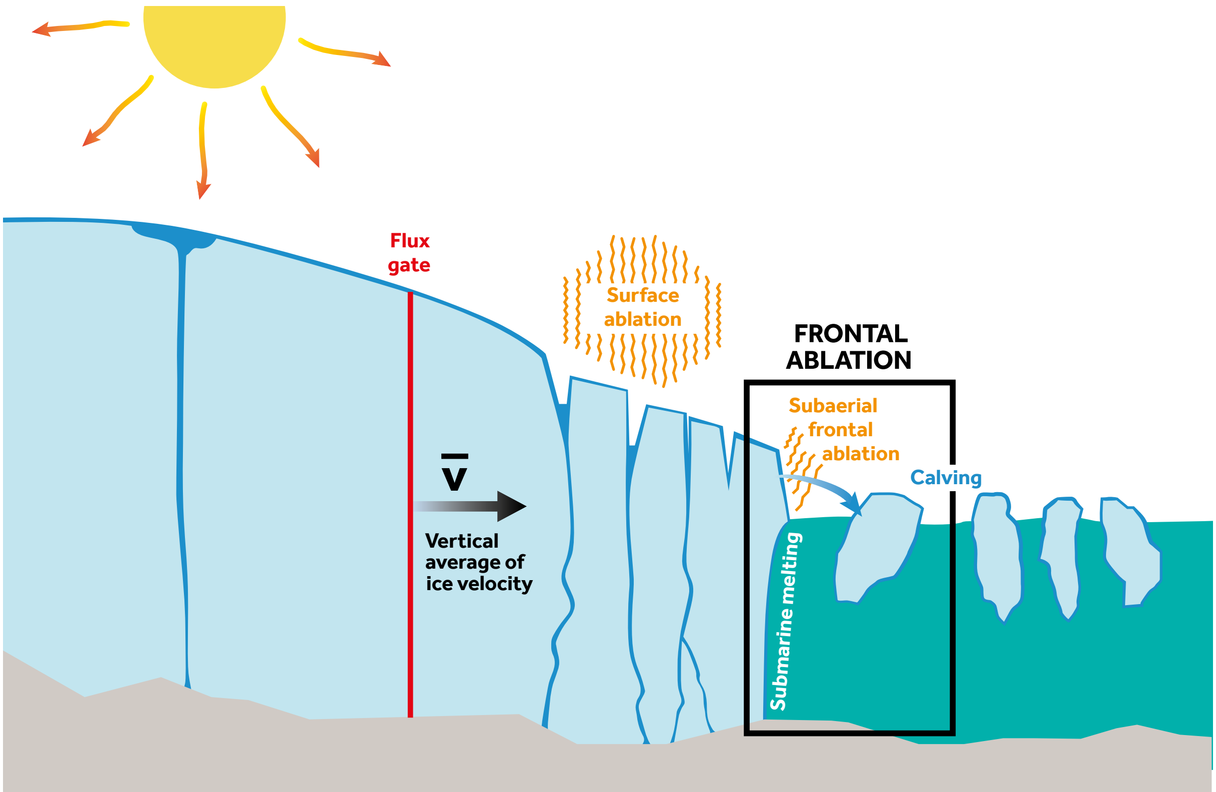


Figure 2. Illustration of typical mechanisms of mass loss at the front of a tidewater glacier. In the case of a floating glacier tongue or an ice shelf, there would also be submarine meting under the tongue or the shelf. Frontal ablation encompasses iceberg calving and submarine and subaerial frontal melting. Surface ablation includes surface melting (and subsequent runoff) and sublimation.

SOURCE: Javier Lapazaran – Universidad Politécnica de Madrid

and subsequent runoff to the ocean is an important mechanisms of mass loss for all landed ice masses except the very high mountain glaciers and the Antarctic Ice Sheet, where surface temperatures are too low for melting except on the Antarctic Peninsula and some coastal areas during the summer. Sublimation is the dominant mechanism of mass loss in very cold environments where surface temperatures rarely reach the melting point, even in summer. Although sublimation is actually a mass loss to the atmosphere, in the end, upon condensation and precipitation, it feeds the ocean. Note that not all glacier ice that melts at surface ends up on the ocean. An important fraction of the surface melting, especially that produced at the accumulation zones of glaciers and ice sheets, percolates through the snow and firn[2], and then refreezes. Also, it can remain during the winter in the form of firn aquifers, as has been observed in certain accumulation zones of southeast Greenland (Foster at al., 2013). In Greenland as a whole, during 1960–2014 only around half of the surface melt ran off (Steger et al., 2017). Even part of the meltwater leaving the glaciers can sometimes not reach the ocean. For example, in High Mountain Asia some proportion of the glacial meltwater is taken up by aquifer recharge and irrigation, especially in the cases of closed drainage basins (Brun et al., 2017).

For the glaciers and ice sheets ending on sea or lake, iceberg calving and submarine melting at the glacier front and under the floating ice tongues and ice shelves is another important mass loss mechanism, especially in the polar regions. Although calving and submarine melting are physically distinct mechanisms, in practice it is very difficult to estimate their separate contributions. For this reason, they are often grouped together under the term ice discharge[3], which is much easier to measure (commonly, using

[2] *Firn* is the term used to denote the material at intermediate stages between snow and ice. Snow that has survived at least a winter becomes firn. Firn becomes ice when the air bubbles between the ice crystals become disconnected, which happens at a pressure of ~840 kg m³.

[3] A related term is *calving flux*. This refers to ice discharge through a flux gate close to the calving front minus the mass change resulting from the advance or retreat of the glacier terminus.

	Projected sea level rise (m)		Glacier & ice-sheet contribution 2015–2100 (m)		
Scenario	2081–2100	2100	Glaciers	Greenland ice sheet	Antarctic ice sheet
RCP2.6	0.39 (0.26–0.53)	0.43 (0.29–0.59)	0.094 ± 0.025 22 %	0.07 (0.04–0.12) 16 %	0.04 (0.01–0.11) 9 %
RCP8.5	0.71 (0.51–0.92)	0.84 (0.61–1.10)	0.200 ± 0.044 24 %	0.15 (0.08–0.27) 18 %	0.12 (0,03–0.28) 14 %

Table 1. Global mean sea level rise with respect to the average value for 1986–2005 under Representative Concentration Pathways (RCP) emission scenarios 2.6 and 8.5, and glacier and ice-sheet contribution for 2015–2100 and their shares of the total projected global mean sea level rise in 2100 (IPCC, 2019, SPM-B1.1, B1.2 & B3.1, §4.2.3).

remote sensing techniques), by computing the mass flux through flux gates close to the calving fronts, or at the grounding lines[4] in the case of floating tongues or ice shelves. This mass flux is computed as the glacier velocity (often measured from satellite synthetic aperture radars or optical imagery) times the section of the flux gate (normally measured using ground-penetrating radar techniques) and times the ice density. These losses largely depend on the glacier velocity, and thus glacier flow acceleration results in increased losses, and associated thinning of the zones from which the glacier ice was drawn. For this reason, they are also referred to as dynamic thinning.

The Antarctic Ice Sheet mass loss is largely dominated by dynamic thinning, which in recent decades has become especially relevant in the western part of the ice sheet (in particular, the Amundsen Sea Embayment) and the Antarctic Peninsula region. In the first case, driven by an increase in sub-ice shelf melting due to the advent of relatively warm Circumpolar Deep Water (Jenkins et al., 2018) and, in the second, driven by the disintegration of certain ice shelves and its associated reduction or loss of ice-shelf buttressing over the outlet glaciers feeding the shelves (Reese et al., 2018). In the case of the Greenland Ice Sheet, mass losses during recent decades have been approximately balanced between dynamic thinning and surface melting and runoff, but in recent years the latter have become dominant, accounting for 42 % of losses for 2000–2005, 64 % for 2005–2009 and 68 % for 2009–2012 (Enderlin et al., 2014). The processes behind incursions of warm water in coastal Greenland that force glacier retreat, and the response of glaciers

NASA/Jeremy Harbeck 2016

Sea-ice loss does not contribute to rising the sea level, as the lower density of ice compared with water is the reason for its flotation. Therefore, when sea ice melts to become water again it occupies less volume, exactly equal to that of its submerged part when it was ice. For the same reason, neither the melting of floating ice tongues or ice shelves contributes to rising the sea level. However, the collapse of ice shelves contributes to the acceleration of the outlet glaciers feeding the ice shelves, hence indirectly contributing to rising the sea level. In the picture, calving iceberg at the Getz ice shelf in Western Antarctica.

«Along the twenty-first century, both thermal expansion of the ocean and mass loss from glaciers and ice sheets will continue to be the main contributors to the rise of the sea level»

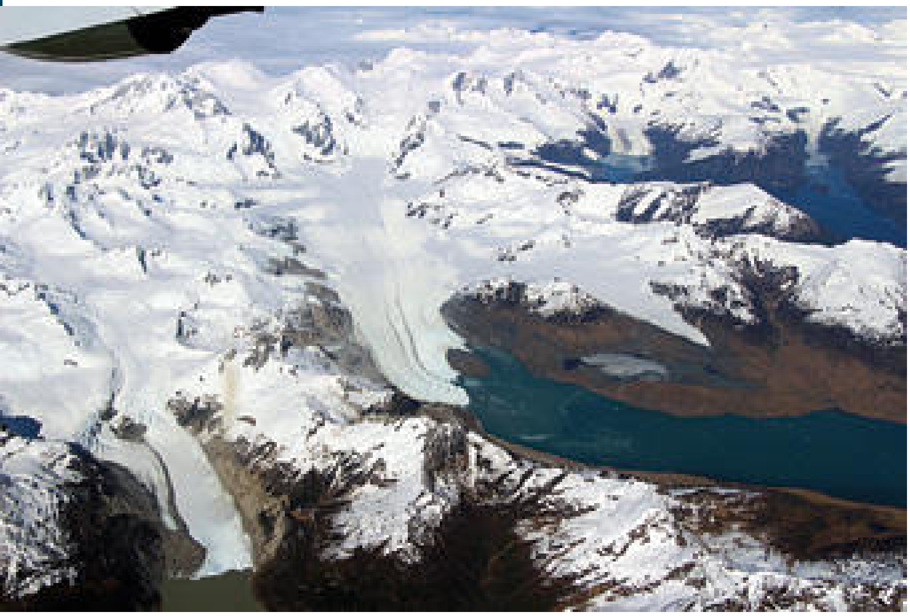
[4] The *grounding line* is the line where a sea-terminating ice sheet loses contact to the ground and becomes a floating ice shelf (or a floating ice tongue, in the case of a sea-terminating glacier).

to ocean forcing, are still poorly understood (Cowton et al., 2018; Straneo et al., 2013).

Though we have focused on mass loss mechanisms, we note that the glacier contribution to SLR results from the net balance between mass gains and mass losses, known as mass balance. The main source of glacier and ice-sheet mass gains is indeed the ocean, through evaporation from oceans, condensation in clouds and snow precipitation over the landed ice masses. Under a warming climate, higher evaporation and subsequent snow precipitation on polar and high-mountain areas is expected. In fact, in Antarctica mass gains due to increased snowfall have partly offset losses by dynamic thinning, in particular in the Antarctic Peninsula (Medley & Thomas, 2018). In Greenland, the decrease in summer North-Atlantic Oscillation following the 1990s has resulted in anticyclonic weather, with reduced cloud cover and snow precipitation, and increased shortwave insolation, which explains most of the post-1990s melt increase (Hofer et al., 2017).

PROJECTIONS OF FUTURE SEA-LEVEL RISE UNDER VARIOUS EMISSION AND CLIMATE SCENARIOS

In the usual IPCC language, the term *projections* is used to refer to predictions of future evolution under assumed greenhouse gasses' emission scenarios.



NASA/John Sonntag 2016

Glaciers have much shorter response time to climate changes compared with ice sheets, due to their significantly smaller size. In the picture, mountains, glaciers, moraines, and fjords in the Chilean part of Tierra del Fuego.

Since the IPCC's fifth Assessment Report (AR5), the so-called Representative Concentration Pathway (RCP) scenarios are used. They are labelled after its associated radiative forcing[5] value in 2100 (originally, they were 2.6, 4.5, 6, and 8.5 W/m^2). These RCPs were consistent with certain socio-economic assumptions, but are being substituted by the Shared Socioeconomic Pathways (SSP), aimed to provide flexible descriptions of possible futures within each RCP. Together with the SSPs, additional RCPs (1.9, 3.4, 7) were introduced. RCP1.9 is of particular interest, as it limits global warming to below 1.5 °C, which is the goal of the Paris Agreement. In what follows, we will mostly focus on RCP2.6 and RCP8.5, as low-end and high-end scenarios, to provide a range of possible impacts. It is important to note that the projections that we will discuss in what follows are based on the SROCC (IPCC, 2019), which uses new estimates with respect to those of AR5 only for Antarctica. For glaciers and for Greenland, as well as for thermal expansion of the ocean and land water storage, the projections are identical to those of AR5. The main reason for this is the lack of updated climate simulations from the Coupled Model Intercomparison Project (CMIP) of the World Climate Research Programme (WCRP), which provide information on the evolution of climate and the associated changes in the oceans, glaciers and ice sheets. Results from the CMIP5 were used for AR5. However, new estimates from CMIP6 are not yet available; they are expected to be used in the IPCC 6th Assessment Report (AR6). In the case of Antarctica, several continental-scale estimates of future Antarctic ice loss, under various emission scenarios, have been made since AR5. Even if using CMIP5 results, these models have provided probabilistic information on associated uncertainties, which has allowed a quantitative assessment of the uncertainty in the dynamic mass losses of the whole of Antarctica, which was not possible in AR5. Hence, updated estimates for Antarctic mass loss projections have been included in IPCC (2019).

The projected global mean sea-level rise to the end of the twenty-first century is shown in Table 1. The associated rates in 2100 are 4 (2–6) mm/yr under

[5] *Radiative forcing* is the difference between the solar radiation absorbed by the Earth and the energy radiated back to space.

NASA/John Sonntag 2016

Iceberg calving and submarine melting at the glacier front and under the floating ice tongues and ice shelves are important mass loss mechanisms, especially in the polar regions. In the picture, northern limit of the Getz ice shelf, fed by the DeVicq glacier, in Antarctica. Melting can be observed near the border of the shelf.

RCP2.6, and 15 (10–20) mm/yr under RCP8.5, i.e., they range between close to present and four times as large (IPCC, 2019, SPM-B3.3, §4.2.3). Table 1 also shows the projected contributions to 2100 by glaciers and ice-sheets. The wide range of uncertainty at the end of the century is mostly due to the uncertainty in the projected contributions from the ice sheets, especially in Antarctica.

We note that the total contribution from glaciers to SLR from present till the end of the twenty-first century is still large. However, its rate of contribution along this century and beyond is expected to decrease in comparison with that of the ice sheets, as glaciers' area and volume substantially shrink and many glaciers disappear altogether, especially at the lower latitudes and altitudes (Hanna et al., 2020; Hock et al., 2019). Greenland ice loss during the twenty-first century will be dominated by surface mass losses, rather than dynamic ice discharge to the ocean, regardless of emission scenario, while that of Antarctica will be dominated by dynamic thinning, driven by submarine melt under the ice shelves and the subsequent loss of buttressing that opposes the seaward flow of the glaciers feeding the ice shelves (IPCC, 2019, §4.2.3).

In the case of Antarctica, certain possible mechanisms of dynamic instability require particular attention, as they could produce enhanced ice mass losses to the end of this century and beyond, with associated substantial and rapid SLR. A large fraction of Antarctica, mostly in its western part, and in particular the Amundsen Sea sector, rests on bedrock below sea level and mostly terminates in the ocean, being referred to as marine ice sheet. The floating ice shelves at these margins, when confined within embayments or in contact with bathymetric promontories on the sea floor, exert a back stress opposing the seaward advance of the ice sheet, thus contributing to its stability. However, nowadays a combination of ocean forcing (ocean-driven basal melt causing thinning and retreat of ice shelves) and atmospheric forcing (increased surface melt deepening surface crevasses, and leading to hydrofracturing and eventually to ice shelf collapse) can destabilize the ice sheet. If the grounding line is located on bedrock with slope falling toward the interior of ice sheet interior, a positive feedback can be triggered resulting in progressively enhanced ice flow to the ocean. This is known as marine ice sheet instability (MISI). Since AR5, there is growing evidence of accelerated retreat compatible with the MISI hypothesis in several major glaciers in the Amundsen Sea sector of West Antarctica, including Thwaites and Pine Island glaciers, and also in Totten Glacier in the Wilkes Land of East Antarctica. This accelerated retreat, however, is not definitive proof that MISI is underway, so the IPCC (2019, Cross-chapter Box 8, §4.2.3.1.2) assesses its level of confidence as *medium confidence*, regarding both the present situation and its future evolution.

Upon disappearance of ice shelves, ice cliffs can be formed, which will be unstable if their heights are sufficient to produce stresses exceeding the strength of the ice. Cliff failure would lead to ice sheet retreat. This process is known as marine ice cliff instability (MICI) and could have the potential to cause partial collapse of the West Antarctic Ice Sheet in the coming centuries. However, there is limited evidence to confirm the occurrence of MICI in the present or in the past, as well as low agreement on the physical mechanism of MICI, so its potential future impact is very uncertain (IPCC, 2019, Cross-chapter Box 8, §4.2.3.1.2).

IPCC (2019) also includes projections for long-term scenarios, beyond 2100, with results from model studies indicating multi-metre SLR by 2300.

«Expected impacts from the rise in sea level include coastal erosion and flooding, which will be exacerbated under climate warming»

In particular, the projected cumulative SLR to 2300 is of 0.6–1.07 m under RCP2.6 and 2.3–5.4 m under RCP8.5. Regarding the contributions from glaciers and ice sheets, all studies coincide in that the glacier contribution will be of limited importance, as, by then, they will have lost much of its mass and many glaciers will have completely disappeared. Concerning the contribution from the ice sheets, there are notable discrepancies among the results from the various studies, which are accompanied by large uncertainties. The latter are mostly related with the expected effects of dynamic instability processes such as MISI and MICI, which could imply a partial collapse of the West Antarctic Ice Sheet. Accordingly, the level of confidence of these results is rated by IPCC (2019) as *low confidence*. We note that there are also studies indicating an stabilising effect by solid-Earth processes that would exert a negative feedback on retreat. These processes include viscoelastic bedrock uplift upon strong decrease of the overlying ice mass, and gravitational effects reducing the water depth at the grounding line. However, their effects on the grounding line retreat are expected to be minimal until after ~2250. Moreover, it is not known how the uncertainties on the lateral variations of the Earth's viscosity structure under the Antarctic Ice Sheet could impact these results. Consequently, these possible stabilizing effects are only expected to weakly slow-down SLR over the twenty-first century, although they could become important on multi-century and millennial time scales (IPCC, 2019, §4.2.3.1.2 & 4.2.3.5).

For Greenland, sustained surface warming might lead, in the long term, to significant,

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The Greenland Ice Sheet is currently losing mass at roughly twice the rate of the Antarctic Ice Sheet, though this could change in the coming centuries. In the picture, northern limit of the north-western marine ice of the Weddell sea, in the Antarctic ocean, where the Weddell Gyre transports marine ice several hundreds of miles northwards. When it approaches open ocean, the waves break up the ice in smaller chunks like the ones in the picture.

perhaps irreversible, retreat of the ice sheet as a consequence of two positive feedback mechanisms. On one hand, the elevation-surface mass balance feedback, consisting in increased surface melt as the surface of the ice sheet evolves to lower and warmer elevations, further increasing ablation. On the other, the albedo-melt feedback, whereby melt increases by the higher heat absorption due to the darkening of the ice surface by the presence of liquid water, reduction of the extent of summer surface snow cover (and increase of that of bare ice) and biological processes. However, the amount and duration of warming required to trigger an irreversible retreat is highly uncertain (IPCC, 2019, § 4.2.3.5).

CONCLUDING REMARKS

As we have seen, the global mean sea level is expected to increase at an accelerated rate over the twenty-first century and beyond, with important impacts on low-lying coastal areas and islands, which are home to many human communities and sustain a variety of ecosystems. Moreover, sea-level rise is not uniformly distributed geographically and, in certain regions, adds up to terrain subsidence due to over-extraction of groundwater, making these zones prone to even more important impacts. Expected impacts from SLR include coastal erosion and flooding, which will be exacerbated, under climate warming, by intensified marine heatwaves, and associated extreme meteorological events, as well as by extreme wave heights. All of these impacts and associated risks are amply discussed in IPCC (2019, Ch. 4–9), which also analyses mitigation and adaptation strategies.

Along the twenty-first century, both thermal expansion of the ocean and mass loss from glaciers and ice sheets will continue to be the main contributors to SLR. Beyond the twenty-first century, the progressive absorption of heat by the ocean will further contribute to SLR for several centuries. The largest uncertainty on long time scales corresponds to the contribution by the ice sheets. Regarding the latter, all models agree that only low-emission scenarios, like RCP2.6, will be able to prevent substantial future ice loss.

The specific paths of future evolution may depend to a high extent on whether certain tipping points are reached or not, and, if reached, on its timing. The two most critical tipping points are, first, the threshold at which the combination of elevation-surface mass balance and albedo-melt feedbacks might cause irreversible retreat of the Greenland Ice Sheet, and second, the thresholds for surface melt and submarine melt under the ice shelves in West Antarctica that might trigger irreversible retreat of the ice sheet, involving MISI and possibly MICI processes. The chance of surpassing these tipping-point is of course much higher for RCP8.5 than for RCP2.6. On millennial time scales, both ice sheets have tipping points at or slightly above the 1.5–2.0 °C threshold (Pattyn et al., 2018). RCP1.9 would therefore be the ideal scenario, as it keeps global warming under 1.5 °C, in agreement with the goals of the Paris Agreement.

In conclusion, SLR on centennial and millennial time scales is critically dependent on the emission scenario considered, emphasising the importance of mitigating the emissions of greenhouse gases for minimising the impacts and risks associated to sea-level rise.

NASA/Jefferson Beck 2018

Large tabular icebergs between the Larsen C ice shelf in Antarctica and iceberg A-68, which collapsed from Larsen C in 2017. The loss of mass of the Antarctic ice sheet is predominantly caused by dynamic thinning, which has become especially important in recent decades in the western section of the ice sheet (mainly in the Amundsen Sea Embayment) and in the Antarctic peninsula.

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INVISIBLE POLLUTION

Emerging marine pollutants

BELÉN GONZÁLEZ GAYA

Since the start of the Anthropocene, the planet has been threatened by a number of risks associated with human activity. Among them, chemical pollution is posing conceptual and technical challenges that are particularly difficult to characterise on a global scale. We must ask ourselves, what is a pollutant? What properties are relevant in their definition? Studies on the abundance, persistence, mobility in the environment, and bioaccumulation potential of the chemical compounds we use every day are changing the paradigm of what we consider pollutants. Thus, compounds that do not cause acute toxicity can still be dangerous for the ecosystem when they continually reach the environment, exist in very high concentrations, or disperse easily. Thus, raising awareness about the forgotten pollution that we unknowingly generate but which is affecting our oceans will be essential to protect the planet.

Keywords: emerging pollutants, suspect analysis, non-directed analysis, transport of pollutants, exposure.

THE RELEVANCE OF UNKNOWN POLLUTION

Since it was accepted that we live in a new geological age, the Anthropocene, in which humans are the main agent that affects the configuration of our planet's ecosystems, the risks and modifications we have subjected it to have been classified in different ways. The concept of *planet boundaries* proposed by the team behind the Anthropocene theory, Johan Rockström and his collaborators (Rockström et al., 2009) included nine great problems or environmental control variables that they theorised could lead to abrupt and irreversible change in continental or even planetary-wide ecosystems if pushed over a certain tipping point (Figure 1).

The threats they identified were 1) climate change, 2) ocean acidification, 3) stratospheric ozone levels, 4) nitrogen and phosphorus cycle disruption, 5) the use of surface freshwater, 6) changes in land use, and lastly, 7) biodiversity loss. They also included two more issues which are not currently quantifiable because, according to the authors, we do not yet know enough about them to be able to estimate their value or to establish characterisation methods that could help us set limits that would maintain the stability of planet Earth. Interestingly, these last two planetary-wide problems are also related to pollution: 8) chemical pollution and 9) atmospheric aerosol loading.

«We cannot establish limits to the production and presence of chemical pollutants, because we do not know how to measure them on a global scale»

In the words of Rockström and his team, «there is not yet an aggregate, global-level analysis of chemical pollution» (Steffen et al., 2015), which makes it extremely difficult not only for large-scale identification, but also for global assessment. Going a little further, a more recent revision of his theory defends the hypothesis that it is impossible to quantify and delimit the concept of *atmospheric aerosol loading*. They also modified the concept of *chemical pollution*, renaming it *novel entities*, thus making this limit even more blurry and vague (Steffen et al., 2015). We cannot define what chemical

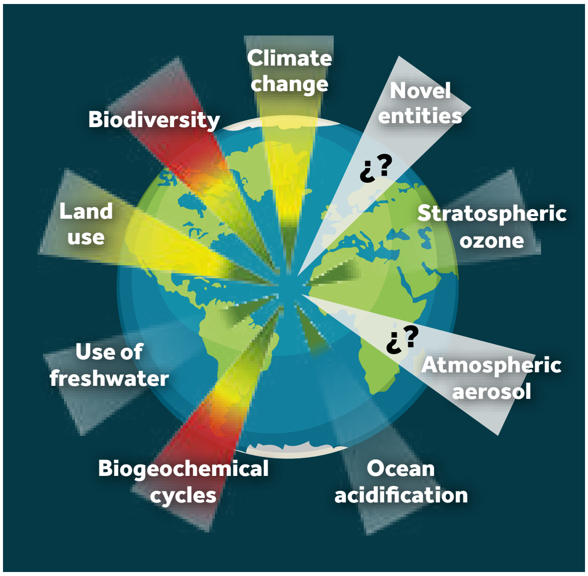


Figure 1. Current state of the nine environmental boundaries, a concept that evaluates the threat of different planetary issues. The threats shown in red have already exceeded the area of uncertainty and so, represent a high risk. Threats shown in yellow are currently in the area of uncertainty and so their risk is growing. Threats that are currently below the established limit are shown in green. Lastly, threats shown in grey (new forms of existing substances and atmospheric aerosols) have unquantified boundaries.

SOURCE: Modified from Steffen et al. (2015)

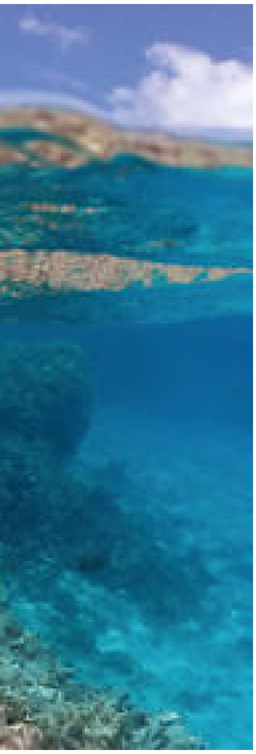
NOAA/PIFSC/HMSRP

At present, humans are the main agent that affect the configuration of our planet's ecosystems. Among the risks associated with human activity, chemical pollution is invisible and difficult to quantify and this poses conceptual and technical challenges.

pollutants – or these new forms of existing substances – are, and consequently, nor can we establish limits to their production or presence because we do not know how to measure them on a global scale. In other words, there is currently no globally accepted scientific methodology that allows us to assess the state of our planet in terms of chemical pollution.

Such ignorance or disagreement regarding the characterisation of these threats is because, in part, of the difficulty in conceptually identifying polluting substances. We do not currently know what does and does not constitute a pollutant. In our collective imagination, a chemical pollutant is understood as a toxic or dangerous substance that is harmful to the environment and its inhabitants, including humans. However, this paradigm is changing in the scientific world. Large-scale use and production of countless substances that would not – in principle – be considered pollutants turns commonly used compounds such as caffeine, perfume, or sweeteners into threats to the most vulnerable ecosystems. In other words, compounds with no apparent harmful effect on the environment can become a threat to our planet's health as a result of their mass use. Nowadays, these compounds, alone or in combination with hundreds of other substances, can potentially be found in extremely high concentrations in our water, land, or air. This is the reason why the classic twentieth-century idea of «pollutants», identified primarily as pesticides, hydrocarbons, or heavy metals, among many others, has now been modified. Thus, the lists of «emerging pollutants» has been broadened to include toiletries and personal care compounds, as well as drugs and food additives, and other chemical substances. These are not new synthetic products, but rather, they are well-known substances that are starting to seem dangerous now that their presence in the environment is out of control. The term *contaminants of emerging concern* may be the one that best definitions for this change in focus. This is because it references our new attention to compounds that are not necessarily new but were not traditionally monitored or studied, are not currently regulated, and are potentially harmful to ecosystems and human health because of their abundance in the environment.

In recent years, the main regulatory agencies, such as the European Union or the US Environmental Protection Agency (EPA), have proposed lists of candidate compounds and recommend monitoring certain common substances such as hormones, drugs,



food additives, and UV filters. These compounds also tend to share a chemical feature that affects their environmental distribution: they are generally more polar than other toxic substances studied in the past; i.e., they have a greater affinity for water. This makes them spread more easily through aquatic systems and so, even if they have a lower tendency to accumulate in fatty tissues and are less toxic, they have very a high dispersal potential in rivers and oceans (ECHA, 2016; European Parliament, 2013, 2015, 2018; UNEP, 2017; US EPA, 2015).

Therefore, it is especially necessary to control these compounds in aquatic ecosystems which are particularly sensitive to the continuous input of urban, industrial, and agricultural waste containing significant concentrations of these supposedly «low danger» substances which can spread very easily. This effect is exacerbated if we consider that sewage treatment plants are not very effective – when they even exist – because they are not designed to extract these types of compounds. Therefore, regulations (and scientific interest in this global change) are increasingly focusing on polar pollutants (those that more easily dissolve in water), with more widespread use and a greater potential for mobility. This indicates that, although the specific pollutants that pose a risk remain unknown, effort is being made to investigate their presence, usage profile, the characteristics that can make them particularly dangerous, and their potential for dipersal through the environment.

HOW CAN WE MEASURE THE UNKNOWN? NON-DIRECTED ANALYSIS

At this time of global change in which «still unknown» pollutants are gaining the recognition they deserve, a number of technical questions have also been raised regarding their quantification in environmental samples. In this sense, mass spectrometry analysis techniques are gaining importance. These allow the molecular identification of substances found in the environment. In addition, the use of spectrometry together with liquid and gas chromatography allows experts to separate these analysed compounds according to their polarity or volatility, respectively, thereby simplifying and improving the sensitivity of the molecular identification process. That is, we are now able to discover more pollutants and identify them at lower concentrations. This analytical equipment has been used for *directed analysis* since the end of the last century; in other words, when we already knew what we wanted to quantify and targeted these substances of interest using chemical standards to confirm and quantify them. For example, if we wanted to study the presence of a pesticide such as DDT in remote areas like the open ocean or Antarctica, water samples were collected in those areas, were analysed using gas chromatography and mass spectrometry, and the results were then compared with the DDT standard; when the target was identified in the sample, it was quantified.

However, how can we quantify something when we do not know what we are looking for? What could be polluting our oceans? Among the millions of substances we pour into the seas, which substances are present in a given area? Which ones are affecting the sea? This paradigm shift requires new techniques, especially in terms of analytical and computational processes, for non-directed analysis of the suspects. We require technology that will allow us to identify the pollutants present in the environment without specifying which substances we want to quantify. The empirical data generated with such techniques would represent a major scientific advancement because they would prevent the bias of only monitoring certain chemical compounds (preselected with varying degrees of success). It would also imply savings in terms of the use of chemical standards, because the acquisition of standards from absolutely every substance which might present a risk to the environment would be completely unaffordable to any research laboratory (Figure 2).

«Compounds with no apparent harmful effect on the environment can become a threat to our planet's health»

Suspect analysis involves some degree of preselection of the pollutants to be measured in water, air, sediments, or biological samples, because it starts from a preconceived list of molecular masses that could potentially be present. In this sense, specific databases are being configured to facilitate these analyses: for instance, xenobiotic compounds in rivers; drugs and abuse substances in sewage treatment plants, or bioaccumulative pesticides in wildlife. These databases include the mass of these compounds, as well as their molecular formula, isotopic profile, structure, and potential fragmentation (how the molecule would break up if analysed in a spectrometer, which is intrinsically

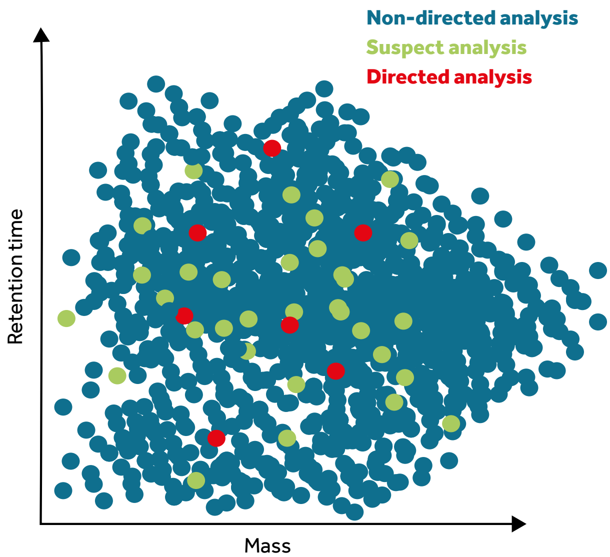


Figure 2. Representation of the myriad of compounds that can be found in an environmental sample analysed through liquid or gas chromatography (LC and GC, respectively) and mass spectrometry, ordered according to their mass and chromatographic retention time (which is related to LC polarity or GC volatility), as measured in arbitrary units. These techniques prevent the bias of monitoring only certain chemical compounds (preselected with varying degrees of success), as shown in this theoretical image which compares the results of the non-directed analysis with those from the suspect analysis.

SOURCE: Author

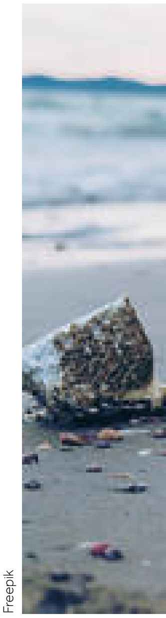
different for each substance), all of which would allow the almost unequivocal identification of the pollutants in a given sample from the environment.

On the other hand, purely non-directed analyses do not use any such databases and so their computational requirements are very demanding because they have to process the millions of substances that might be present in each sample whilst simultaneously characterising and differentiating which ones are synthetic or natural, dangerous or harmless, and endogenous or exogenous. These techniques are still being developed and so, for the moment, suspect analysis is still the most scientifically accepted technique when applied in studies using candidate lists with thousands or tens of thousands of compounds.

FROM OUR HOMES TO THE OPEN OCEAN

While it is true that the chemical properties and toxicity potential of the immense number of chemical substances we use is still being characterised, everyone knows that humans are the main source of these pollutants (evidently, because many of them are synthetic or anthropogenic derivatives of natural products). Pollution is produced mainly by our industry, agricultural and livestock farms, and transport and energy production systems. However, especially since the acceptance of contaminants of emerging concern, they are also produced in our hospitals, kitchens, bathrooms, and household appliances. Leaving aside the most well-known industrial and agricultural pollutants, the potential effects of a broad variety of consumer products when released into the aquatic environment in large concentrations or on continous release are currently under consideration.

Some of the applications of the pollutants that are currently under the scientific scrutiny are those which increase the safety or improve the physical and chemical properties of consumer goods. These substances include flame retardants, adhesives, water proofers, non-stick materials, plasticisers or thermostabilisers, cosmetic additives, and gelling agents. Indeed, these compounds are required in several products we use and consider essential. Who does not want their carpet or sofa to be protected from a potential fire? Or have mountain boots and raincoats that shield them from the rain? However, the scientific community is calling for the more rational use of these substances, for their replacement when alternatives are



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Greenpeace / Marco Care

«Aquatic ecosystems are particularly sensitive to urban, industrial, and agricultural waste»

Noel Guevara / Greenpeace

While plastic waste at sea provides visible and often shocking pictures, chemical pollution tends to go unnoticed to the general public. For this reason, the availability of more powerful informational and regulatory tools is important.

«At this time of global change, several technical questions regarding the quantification of contaminants in environmental samples have also been raised»

available, and for proper management and monitoring of their potential effects in the environment.

These characteristics are very practical and desirable in consumer goods, but they also generate potential risks when released into the environment. On the one hand, most of them are man-made, synthetic substances which were not previously present in nature; even if they are organic (principally comprising hydrogen and carbon), they do not usually degrade easily because no organisms or bacterial communities can use them as a regular source of carbon. On the other hand, many of these substances are also specifically designed to be durable to protect us from the rain, prevent our food from sticking to pans, and protect our computers and phones from fires for as long as possible. That is, most of them were designed to be recalcitrant. However, contaminants of emerging concern are not always so persistent; pharmaceuticals or food additives, for instance, have shorter degradation times. Nonetheless, their continuous production and consumption in our everyday lives means that, inevitably, these still reach the environment and accumulate there. In addition, as mentioned above, the polar or semipolar chemistry of these contaminants makes water their main transportation route. Considering that more than 70 % of the Earth's surface is oceanic, the seas are the main sink for commonly used chemicals, and their effects on these ecosystems remains unknown.

It is also noteworthy that both agricultural and domestic neo-contaminants end up or accumulate in wastewater. Pesticides and fertilisers are flushed with irrigation or rainwater and accumulate in aquifers or join the runoff water that reaches riverbeds. The water from washing our non-stick frying pans, plastic food packaging, and waterproof clothing, the sweeteners, and drugs we consume and metabolise, personal hygiene products and toiletries all end up in sewage water. In the best-case scenario this water ends in sewage treatment plants, but even these cannot degrade these compounds before they are dumped into rivers and seas because, as already mentioned, they were simply not designed for this purpose. Sewage treatment plants are an ideal location to maximise the benefit of monitoring and removal techniques. The main regulations are applied in this area, and a lot of scientific work is currently using suspect and non-directed analyses to look for specific compounds that do not degrade well in treatment plants, leading to their systematic release. Sewage treatment plants often apply primary treatments, using physical techniques to separate solids and fats, and secondary treatments using bacteria (activated sludge, bacterial beds, biodiscs, etc.) to trigger biological processes that eliminate most of the organic matter. However, of course, these processes do not affect compounds that are resistant to bacterial degradation. Tertiary treatments (chlorination, ultraviolet radiation, etc.) primarily intend to remove potential pathogens from water so that it can be used for irrigation or, for instance, for urban cleaning. However, these treatments are not specifically designed for chemical decontamination and are only applied in 27 % of Spanish sewage plants, according to the Spanish Desalination and Reuse Association (AEDyR, 2019). Therefore, the most abundant synthetic compounds have a higher probability of ending up in the environment without their prior transformation. Lastly, discharging treated waters directly into coastal areas is a common practice; treatment plant's effluents currently drop these «invisible» and unknown substances (whose combined effects we do not yet understand) into the marine ecosystem via our beaches or through sewage outlet pipes several hundred metres off the shore.

The fact that the results obtained from sewage effluents or from indoor contaminant studies (carried out in domestic or working environments, among other locations) are increasingly coinciding with those reported from the Great Lakes in Canada, the open ocean, or even from Antarctica's wildlife is quite self-explanatory (Aznar-Alemany et al., 2019; Besis & Samara, 2012; Deblonde et al., 2011; Klečka et al., 2010; Roscales et al., 2016). The spread of these contaminants generated in environments of human influence appear to have no limits. If we do not impose measures to stop their release into the environment, the consequences for global ecosystems could be disastrous.

LEARNING TO AVOID UNKNOWN ENEMIES

Some pollutants are recognised by everyone today, the most obvious being plastics (although plastic is a solid residue, not a chemical contaminant, which is the focus of this text). Public messaging promoting the return, reuse, recycling, and proper disposal of plastics is increasing. Others pollutants are less well-known, even when information about them is available and they are the subject of public awareness campaigns. The fact that they are not

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The spread of pollutants generated in environments of human influence seems to have no limit. The pollutants found in domestic or working environments are the ones that are most frequently reported in the open ocean or even in wildlife in Antarctica.

«A wide range of consumer products are currently under consideration for their potential effects when released into the aquatic environment»

«visible», or that their effects might not be as evident or instantaneous as a loggerhead turtle trapped in a plastic bag, makes chemical contaminants of emerging concern go even more unnoticed to the general public. Unlike solid waste such as plastics, chemical pollution cannot be seen with the naked eye. Therefore, more powerful informational and regulatory tools are required, and even when implemented, these are not always as effective among consumers as expert scientists would like.

A recent example of public awareness is that of perfluorinated compounds. These are substances containing fluoride (which makes them very persistent) and whose applications include food packaging insulators, protective coatings for furniture and automobiles, cosmetics, waterproof clothing and mountain accessories, adhesives and sealants, and fire foams, etc. In particular, perfluorooctane sulfonate (PFOS) and its salts, as well as perfluorooctanoic acid (PFOA), have been regulated by the Stockholm Convention (since 2009 and 2017, respectively) which mandated the cessation of their use for non-essential purposes. The Madrid Declaration of 2015 also recommended monitoring them and stopping the production of some of these compounds (Blum et al., 2015). Given the toxic and bioaccumulative effects of these substances and their capacity for long-distance transport in the environment, this declaration was signed by hundreds of scientists. While production in the United States and in Europe has ceased or is in the process of doing so, China still supports their use in applications with no alternative options or where there is no commercial or political will to stop (because of increased cost or because the change might require some degree of industrial adaptation). On the other hand, some well-known brands of furniture, clothing, mountain equipment, cosmetics, appliances, and kitchen tools, as well as other products that traditionally used these compounds have already stopped using them and the «PFOA/PFOS-free» symbols are becoming increasingly common. Nonetheless, the presence of these contaminants has already been reported in the atmosphere, water, sediments, and biota of remote locations including in oceans, the Arctic, and Antarctica, and considering that they will remain for tens or hundreds of years, they could be dangerous wherever they accumulate.

«The most abundant synthetic compounds have a higher probability of ending up in the environment without having been significantly changed prior to their release»

Likewise, some flame retardants such as polybrominated diphenyl ethers (PBDE) have become especially infamous. Just like perfluorinates, the structure of PBDEs contains bromine atoms (another halogen element) which makes their molecular bonds especially difficult to break and therefore, very persistent in nature. Some of them (PBDE with four, five, six, seven, or ten bromine atoms) have also been included in the Stockholm Convention, which recommends replacing them in plastic and textile polymers. In addition, their electronics applications have generated huge environmental concern, mainly because of the high demand for mobile phones, tablets, and personal computers which all use them in their components. The correct disposal

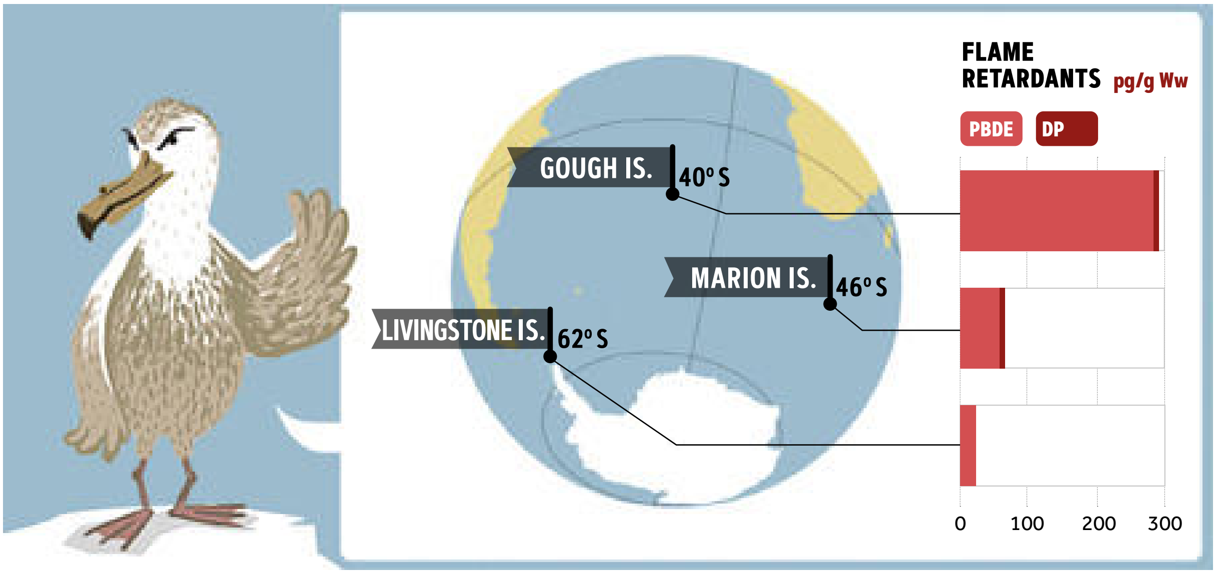

Figure 3. The presence of flame retardants (polybrominated diphenyl ethers or PBDEs and Dechlorane Plus or DP) in giant petrel populations (*Macronectes* spp.) in the South Atlantic Ocean, South Indian Ocean, and Antarctica (Roscales et al., 2016). These retardants are very persistent in nature and are also widely used in mobile phones, tablets, and computers, and so the correct disposal and recycling of obsolete devices is essential to prevent the dispersal of these pollutants in very remote areas such as the Antarctic seas.

SOURCE: Figure courtesy of Roscales et al. (2016)

and recycling of obsolete electronic devices is essential to prevent the dispersal of these pollutants because the transmission of PBDE to wildlife and water has been documented from uncontrolled landfills and urban areas to pelagic birds in very remote regions. These substances accumulate in these organisms through the marine food chain (Figure 3). Fortunately, some very well-known electronics brands are already including this group of toxins in their «substance-free» lists, and given the more recent regulations, PBDE is expected to also be included in these soon.

There are also other groups of plasticisers and polymer modifiers which are more familiar to users because they are used in food and personal and baby products. These include bisphenol, phthalates, and organophosphorated compounds. Regulations are already in place regarding their use in food and personal products, and it is increasingly common to see the labelling of reusable bottles and baby products or children's toys indicate that they are free from these substances. However, as with the previous compounds, some studies have detected them in several matrices and environments including very remote Arctic atmospheres, Amazonian waters, the open ocean, and in large marine mammals (Fu & Kawamura, 2010; Garcia-Garin et al., 2020; Schmidt et al., 2019; Xie et al., 2007).

Although the potential list could be endless (or, at least, the end is still unknown even to the most experienced of scientists), drugs represent another group of substances of emerging concern that are currently being studied in aquatic ecosystems and whose potential effects are still a mystery. The use and abuse of medical and illegal drugs turns sewage treatment effluents into chemical cocktails (with can have synergistic or antagonistic effects) that are directly discharged into rivers or coastal areas. High levels of antidepressants and hormones have been detected in the environment, and these can alter local wildlife, even in protected spaces affected by urban sewage treatment plants such as, for instance, the Urdaibai Reserve – a UNESCO heritage space in Vizcaya, Spain (Mijangos et al., 2018; Ziarrusta et al., 2019). In this regard, it is important to highlight the intended future goal for neo-contaminants. With adequate political and industrial will, some dispensable or replaceable compounds could disappear from our products and, little by little, also from our most sensitive ecosystems. However, this is not the case with pharmaceuticals; their applications protect human health and are paramount and so, while we need to control abuse, self-medication, and compound degradability, ceasing to use them is not an option. Thus, we need to fight for better waste management and for the implementation of adequate technology in our sewage treatment to eliminate and remove these compounds before we return these waters to nature.

Generalitat Valenciana

The processes performed in sewage treatment plants are not designed to remove emerging contaminants and so they are not particularly effective.

Therefore, this the joint responsibility of consumers, producers, global administrations (pollution knows no borders), and the scientific world. We must all collaborate to raise awareness and control, and better manage contaminants of emerging concern because they might be invisible, but they are still important.

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The use and abuse of medical and illegal drugs turns sewage treatment effluents into chemical cocktails. Levels of antidepressants and hormones capable of affecting wildlife have been found in the Urdaibai Reserve in the Basque Country.

«Some dispensable or replaceable compounds could disappear from our products and, little by little, also from our most sensitive ecosystems»

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HOW MUCH WARMER IS THE MEDITERRANEAN BECOMING?

Thirty-five years of satellite observations

MARÍA JOSÉ LÓPEZ GARCÍA

Global warming particularly affects the oceans and seas. In the Mediterranean Sea, in situ oceanographic and meteorological records, together with the most recent satellite observations, show an estimated warming of between 0.6 °C and 1 °C over the last three decades. In this article we present the results of an analysis of a 35-year series of monthly thermal images in the western basins of the Mediterranean. The data indicate an intensification in the summer season: with the summers becoming longer and more intense and the months of June and July recording the highest rates of warming, with increases of 0.6 °C/decade.

Keywords: Mediterranean, global warming, climate change, physical geography, remote sensing.

THE MEDITERRANEAN, A «MINIATURE OCEAN»

The Mediterranean, a semi-enclosed sea framed by three continents, is a unique setting. It occupies only 0.7 % of the world's ocean surface and 0.3 % of its volume of water, but is considered by many authors as a «miniature ocean», a perfect laboratory for studying climate and hydrological patterns (Bethoux et al., 1999), because many phenomena observed in the oceans also take place in the Mediterranean. The configuration of its basin, which has large topographical contrasts, and its intermediate position between temperate and subtropical climates make this sea a particularly sensitive area and it has, therefore, been identified as a climate change hotspot.

«The Mediterranean is a particularly sensitive area, identified as a climate change hotspot»

The Mediterranean can be defined as a «concentration basin» where water losses through evaporation (outputs) exceed gains (inputs) from rainfall and rivers. This deficit is compensated by the exchange of marine waters of different salinity with the Atlantic Ocean through the Strait of Gibraltar and, to a lesser extent, with the Black Sea through the Bosporus narrows. Less dense Atlantic water flows through Gibraltar and progresses towards the eastern basin, changing as it flows through; at greater depths, denser Mediterranean water flows out of the eastern part of the basin.

The general pattern of circulation, first described at the beginning of the twentieth century, is thermohaline,[1] i.e., it originates from the differences in density between the different bodies of water. It is structured in three layers (surface, intermediate, and deep) and follows a cyclonic pattern around the western and eastern sub-basins (Figure 1). The Mediterranean is also one of the few places in the mid-latitudes where deep water formation occurs. This is a fundamental process of oxygenation of the deep layers of water which takes place in winter in the Gulf of Lion and the northern Adriatic. In recent decades, the general circulation pattern initially described has been revised and some characteristics of mesoscale circulation and elements of inter-annual variability have been incorporated in the light of increasingly extensive observations and measurements (Bergamasco & Malanotte-Rizzoli, 2010; Millot & Taupier-Letage, 2005).

[1] The term *thermohaline* refers to the temperature and salinity of water masses, which determines their density.

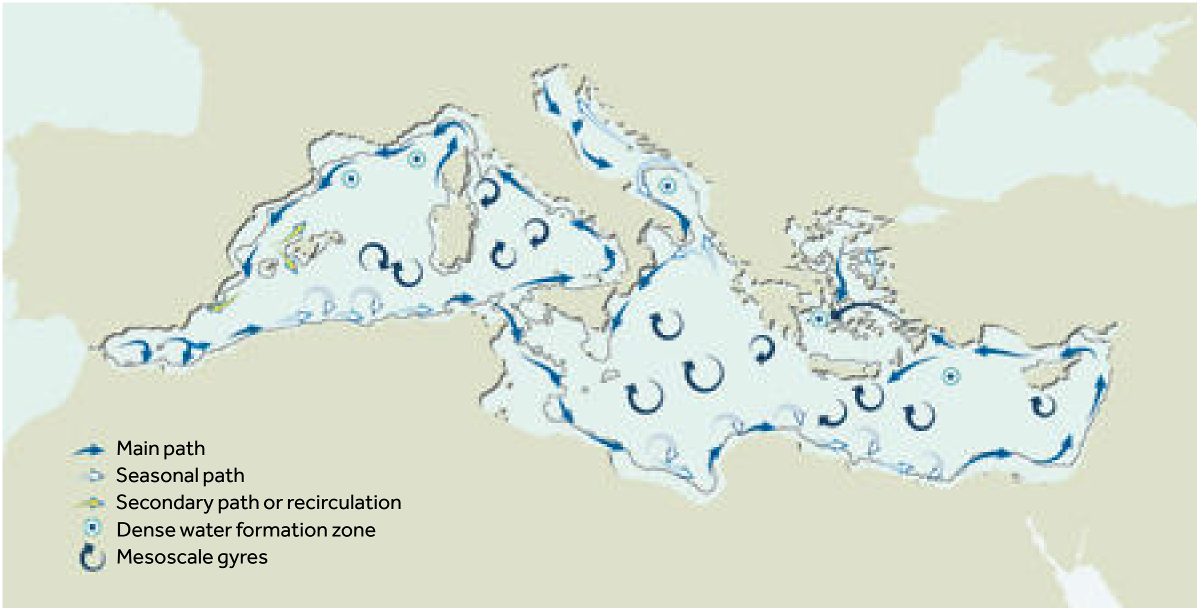


Figure 1. Map of the surface circulation patterns in the Mediterranean (according to Millot & Taupier-Letage, 2005). General circulation in the Mediterranean originates from the differences in density between the different water masses. It is structured in three layers (surface, intermediate, and deep) and shows a cyclonic pattern around the western and eastern sub-basins.

SOURCE: UN Environmental Programme. GRID-Arendal. https://www.grida.no/resources/5915

River inputs are a relevant factor in the hydrological balance of the basin. Only six basins cover an area of more than 50,000 km^2 (those of the Nile, Rhone, Ebro, Po, Moulouya, and Evros) and fifteen others cover 10,000 km^2 each; the rest are small and medium sized, with a short-lived torrential system. The torrential nature of the rivers and the Mediterranean climate, characterised by episodes of heavy rain, often produce floods that have a major impact on human societies. In recent decades, there has been a decrease in river contributions to the basin, partly as a result of climatic causes, but mainly due to human activity, such as the construction of reservoirs and an increase in agricultural consumption. The decrease in river contributions may be one of the factors that could explain the recent increase in the salinity of the deep Mediterranean waters (García-Martínez et al., 2018).

«The main environmental problems we have identified in the Mediterranean are related to the climate and hydrology of the basin itself»

The main environmental problems we have identified in the Mediterranean basin are directly or indirectly related to the climate and hydrology of the basin itself: the scarcity of water resources, frequency of flooding because of the intensification of extreme rainfall, erosion and coastal degradation processes, water pollution from urban and industrial discharges, and forest fires. Human pressure on the shores of the Mediterranean – which has been more intense in recent decades – has ignored the fact that the Mediterranean Sea is an environmental system in which multiple factors interact; any alteration entails impacts on global functioning whose consequences we are far from being able to assess.

RECENT WARMING OF OCEANS AND SEAS

Today, there is a consensus in the scientific community regarding global warming due to the increase in atmospheric CO_2, which has been particularly evident over the past four decades. The *Fifth Assessment Report* (AR5) of the Intergovernmental Panel on Climate Change (IPCC) reported a global warming of 0.85 °C for the period 1889–2012 (IPCC, 2013). On a global scale, it has been estimated that between 1970 and 2010, the oceans had accumulated more than 90 % of the energy increase in the climate system. Global warming is evident in the surface layer, up to 75 m deep, where an average rate of thermal increase of 0.11 °C/decade has been reported.

It is not easy to identify temporal trends in marine ecosystems that can be used to assess the impact that environmental changes, including climate change, are having on them. The paucity of in situ records from marine stations and oceanographic campaigns over long time series, as well as differences in the instrumentation and methodology used in data collection, make retrospective analyses difficult. The measured rates vary depending on the spatial scale (global, regional, or local), area analysed, and time period considered.

Based on the sea surface temperature (SST) databases compiled at the Hadley Centre in the United Kingdom Meteorological Office, several authors identified a period of temperature decline between 1948 and 1970, followed by a continued period of accelerated warming since then (Belkin, 2009; Trenberth et al., 2007). According to these authors, the surface temperature in the Mediterranean increased by 0.71 °C from 1982 to 2006, making this sea one of the areas of the planet classified as «rapidly warming» (together with the Baltic Sea, North Sea, Sea of Japan, and Sea of China), with rates that are 2–4 times that of the global average.

Moreover, recent reports by the Copernicus Marine Environmental Monitoring Service (CMEMS) based on available (in situ and satellite) observations (Von Schuckmann et al., 2018), point to a global oceanic warming of 0.016 °C/year since 1993, with much higher figures for the Mediterranean (0.04 °C/year).

In the Iberian Mediterranean, as well as the intermediate and deep layers, there is no doubt about the increase in surface temperature and salinity. The latest *Cambio climático en el Mediterráneo español* report ("Climate change in the Spanish Mediterranean", Vargas-Yánez et al., 2010) showed an average increase in sea surface temperature for the period 1948–2005 which fluctuated between 0 °C and 0.5 °C, depending on the area of the Mediterranean coast considered; at intermediate depths (200–600 m) the increase was between 0.05 °C and 0.2 °C and in the deep layers, it was between 0.03 °C and 0.1 °C. Although the increase in the deep layers may seem minor, given the high specific heat of the sea, small increases mean that the sea has absorbed enormous amounts of heat. This warming was particularly noticeable from the 1970s onwards.

Systematic maritime observation records in the Iberian Mediterranean were mostly implemented in the 1990s, with the exception of the L'Estartit Oceanographic Station. This station (located on the Catalan continental platform, 4 km from the coast) covers the longest uninterrupted oceanographic series in the Mediterranean because it has been recording data since the 1970s. Based on these observations, Salat, Pascual, Flexas, Chin, and Vazquez-Cuervo (2019) reported a warming rate of 0.03 °C/year in the surface layers, with higher values (0.09 °C/year) recorded for the last decade. The same authors also identified seasonal variations, with higher rates recorded in spring (0.039 °C/year).

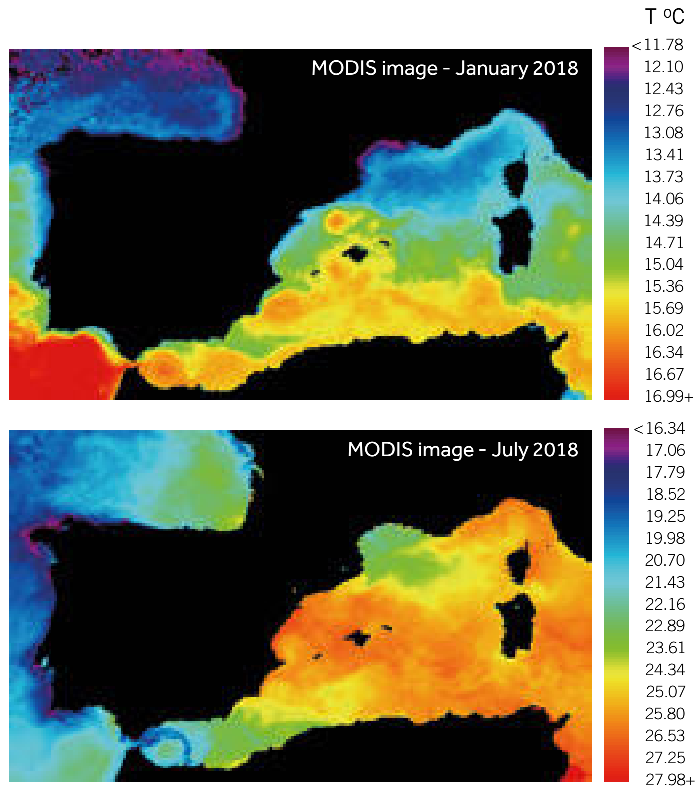


Figure 2. Example of a typical winter (January 2018) and summer (July 2018) scenario for the temperature of Mediterranean waters. In winter, a north-south latitudinal gradient (~4 °C) was observed between the coldest waters in the northern basin and the warmest ones in the Alboran basin. In summer, the spatial temperature variability was greater (~9 °C) and there was a high degree of warming in the central basins. The image shows the area analysed.

SOURCE: Pictures by NASA EOSDIS PO.DAAC (**http://podaac.jpl.nasa.gov/**), processed by the author.

■ WHAT DO THE OBSERVATION SATELLITES TELL US ABOUT THE MEDITERRANEAN?

Since the 1980s, thermal images obtained by the Advanced Very High-Resolution Radiometer (AVHRR) sensor on board NOAA satellites have provided a synoptic and continuous view that complements in situ recordings. The radiation recorded by these sensors is considered representative of the sea surface temperature, a key parameter in climate studies. Over time, other sensors have been incorporated, such as the Moderate Resolution Imaging Spectroradiometer (MODIS),

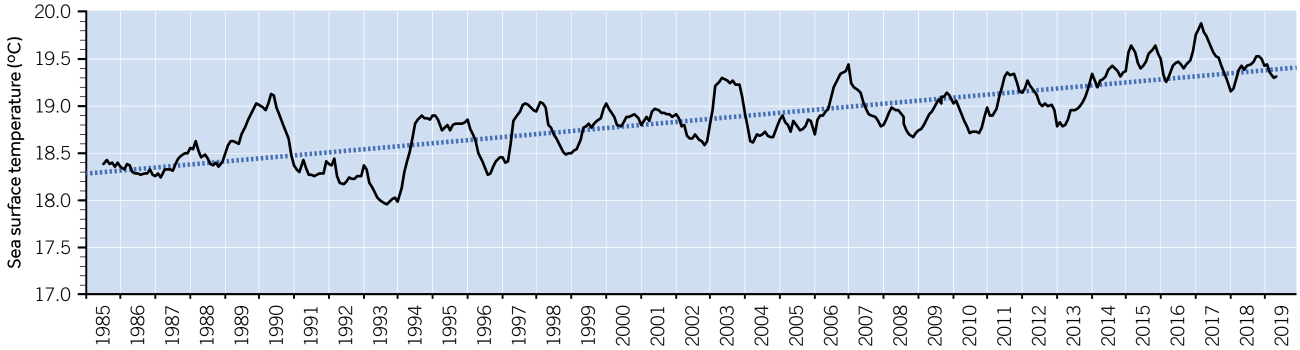


Figure 3. Evolution of sea surface temperature in the Ligurian-Provençal, Balearic, Algerian, and Alboran basins for the period 1985–2019, from thermal images from the NOAA and MODIS satellites. The average heating rate was 0.03 °C/year.

which allows the sea surface temperature and other oceanographic parameters to be accurately inferred.

At the beginning of remote sensing from space in Spain, the PhD dissertation *La temperatura del mar Balear a partir de imágenes de satélite* ("The temperature of the Balearic Sea from satellite images") (López García, 1991), the product of a collaboration between the Department of Geography and the Remote Sensing Group in the Department of Thermodynamics at the University of Valencia, showed the potential of thermal images to gain a better understanding of the hydrology of the Mediterranean and marked the beginning of the research presented here. Thirty years later – with the images having been extensively proved as viable – the availability of image series of sufficient quality and extension and the possibility of contrasting the results with data obtained by other authors, have allowed us to confirm the trends pointed out in previous publications (López García, 2015; López García & Camarasa, 2011). An updated summary of this research is presented below.

«Human pressure on the shores of the Mediterranean has never considered the fact that the sea is an environmental system in which multiple factors interact»

Various studies (López García & Camarasa, 2011; Mohamed et al., 2019; Nykjaer, 2009; Shaltout & Omstedt, 2014; Skliris et al., 2012) based on satellite data have suggested warming rates in the Mediterranean ranging from 0.015 to 0.04 °C/year, depending on the region and period considered. The highest values (0.05 °C/year) were identified in the eastern Mediterranean. In summary, we can say that over the last three decades the Mediterranean Sea has experienced an estimated increase in its global surface temperature of 0.6–1 °C. Some predictions based on these data, and considering the trends of recent years, suggest that this increase could reach 5.8 °C by 2100 (Sakalli, 2017).

Focusing on the Ligurian-Provençal, Balearic, Algerian, and Alboran basins of the western Mediterranean, our analysis covered the series of monthly thermal images available from January 1985 to October 2019.[2]

The average seasonal curve obtained for this series and for the area as a whole shows that the lowest monthly rate was in February (14 °C) and the highest in August (25 °C). However, in some years (August 2003, September 2009, and August 2018) monthly values above 28 °C were recorded at some points in the basin. As an example, Figure 2 shows the spatial variability of temperatures in winter and summer in the different sub-basins. In the typical winter scenario there was a clear latitudinal gradient with colder waters in the Ligurian-Provençal basin and warmer waters in the Alboran basin. The summer situation was characterised by warming of the central basins (Balearic and Algerian) while the waters with an Atlantic influence in the Alboran were always comparatively colder.

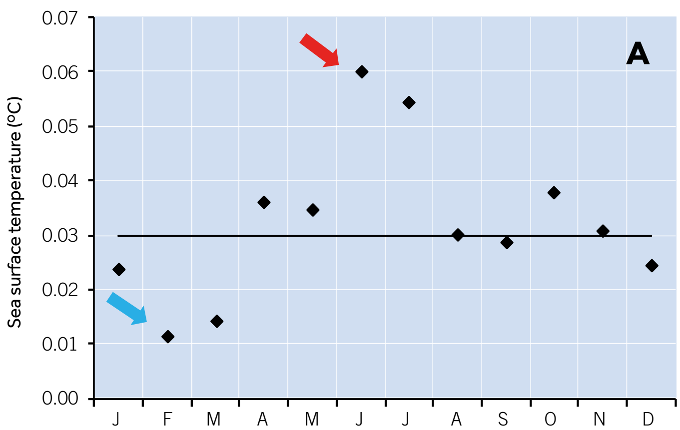
[2] For the 1985–2009 period, the NOAA-AVHRR satellite images from the Pathfinder archive of the Physical Oceanography Distributed Active Archive Center (PO.DAAC) v.5 were used; the 2000–2019 period used images from the MODIS-Terra Level 3 v2014 sensor. In both cases, we analysed night-time images with a spatial resolution of 4 km that had been corrected by algorithms tested and validated by NASA. These data are available online at the Jet Propulsion Laboratory (NASA) (http://podaac.jpl.nasa.gov/). The availability of data from both sources for the period 2000–2009 and their high correlation (r^2= 0.99) allowed the series to be homogenised (López García, 2020).

The recent warming of the Mediterranean is evident from the evolution curve obtained for 1985–2019 (Figure 3) which represents the average temperature calculated for all the basins in each month with a 12-month moving average applied to filter out the seasonal effect. The resulting rate of variation for all the basins was 0.03 °C/year, which represents a total temperature increase of approximately 1 °C over the decades considered in this analysis.

LONGER, WARMER SUMMERS

The calculation of monthly heating rates showed seasonal differences ranging from minimum values in winter (~0.01 °C/year in February and March) to maximum values in spring-summer (~0.06 °C/year in June and July) (Figure 4). These data confirm previously published results (López García, 2015) indicating that warming in the Mediterranean occurs mainly during the spring–summer months, which therefore entails changes in the seasonal curve. While the warming of the sea over the last 35 years is estimated to have been approximately 1 °C, this increase mainly occurred during the months of June and July when the temperature rose by almost 2 °C.

The variations in the seasonal curve can be seen more clearly in Figure 5, which shows the average seasonal curves calculated for the periods 1985–1999 and 2000–2019, together with the monthly temperature increases between both periods in absolute values. In the first decade (1985–1999), the 24 °C average was only exceeded in August, while in recent decades (2000–2019) this occurred in three months (July, August, and September), with monthly averages close to 27 °C recorded in August 2003 and



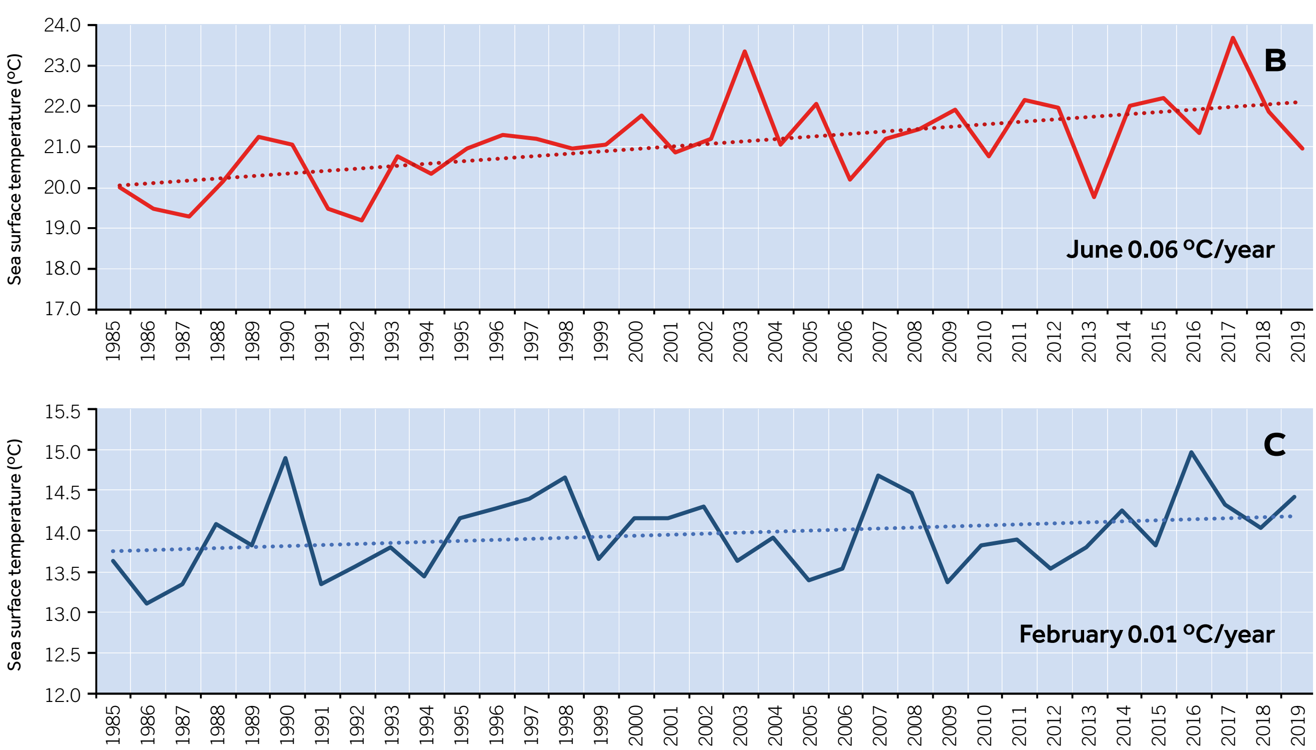


Figure 4. Graph **A** represents the rates of change (°C/year) in sea surface temperature (SST) calculated by month. The lowest values occured in winter (February and March) and the highest ones were recorded in spring-summer (June and July). The horizontal line marks the average annual rate (0.03 °C/year). All the trends were significant (with *p*-values ranging from < 0.0001 to 0.034) except for February, which was not statistically significant. Charts **B** and **C** represent the time adjustments for the months of June and February.

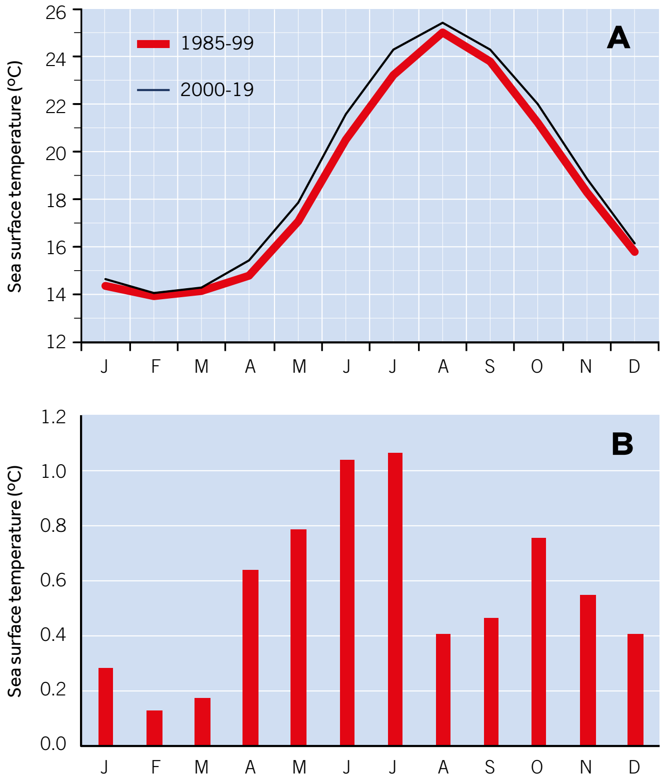


Figura 5. **A**) Average seasonal curves of the surface temperature of the Mediterranean for the periods 1985–1999 and 2000–2019. **B**) Temperature increase per month between both periods. The changes in the seasonal curve show that the summer season was starting earlier and becoming longer, with temperature increases of 1 °C during the summer and 0.5 °C in the autumn between both periods.

2018. These results show that the summer season started earlier and was more intense, with average temperature increases in spring–summer (~1 °C) and autumn (~0.7 °C) over the last two decades.

CONCLUSION

The analysis carried out in the western Mediterranean basins shows that rapid warming has occurred over the last three decades, with an average rate of 0.03 °C/year, which was even higher depending on the Mediterranean region analysed. These figures are in line with those recently published by other authors and confirm the trends noted in previous studies referring to the 1985–2009 period (López García, 2015). Warming in the Iberian Mediterranean took place mainly in spring–summer and autumn, and there was a clear trend towards the anticipation, prolongation, and intensification of the summers.

The consequences of warming in the Mediterranean (Figure 6) in terms of rising sea levels, potential alteration of marine circulation patterns, the abundance, distribution, and structure of marine species, and the frequency and intensification of atmospheric processes such as isolated high altitude depressions, are matters of interest and research for the scientific community, as shown by the IPCC *Special Report on the Ocean and Cryosphere in a Changing Climate* (25 September 2019). While the causality and attribution of these consequences to climate change remain difficult to discern, there is a growing consensus that warming is not a future projection but an obvious reality.

We must reflect upon the role of human beings as the main agents of this warming, but also on our responsibility for the many processes that have altered on the shores of the Mediterranean and in the sea itself: the excessive urbanisation of the coast and alteration of natural coastal ecosystems, agricultural intensification, overexploitation of aquifers, river and marine pollution, and overfishing, among other actions, have impacted and accelerated effects that should not be attributed solely to sea warming.

Pere Pripz/Wikimedia

Figure 6. The consequences of warming in the Mediterranean upon aspects such as the intensification of atmospheric processes such as isolated depressions at high levels are the subject of interest and research by the scientific community. The image shows the consequences of hurricane Gloria in Barcelona; Gloria struck the Mediterranean coast at the beginning of 2020.

Thus, there is a need for greater awareness and the implementation of immediate actions to slow down and mitigate the environmental problems we are facing.

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TOXIC MICROALGAE AND GLOBAL CHANGE

Why have proliferations increased along the Mediterranean coast?

MAGDA VILA, JORDI CAMP AND ELISA BERDALET

The ocean and the continent converge in a very narrow line that is, nonetheless, truly relevant to the health, leisure, and economy of our society. The Mediterranean coastline has undergone major changes over the last fifty years, which is evident in the alteration of its microalgae species. The proliferation of dinoflagellates is now common in microscopic organism communities in this ecosystem as a result of the modifications caused by humans and climate change. The increased frequency with which toxic microalgae blooms are detected has been key to raising awareness of this change.

Keywords: phytoplankton, microalgae, marine toxins, *Ostreopsis*.

MARINE MICROALGAE AND MOBILITY IN A GLOBALISED WORLD

In a globalised and highly communicated planet like the one we live on, human movement from one end of the world to the other takes a matter of a few hours. Goods usually take a little longer, but they can also end up in places far away from their shipping origin in only a matter of days, weeks, or months. As part of this coming and going of people and products, we often also accidentally and involuntarily transport some living organisms, both those visible to the naked eye and others that are microscopic (Hallegraeff, 1998). Here we will focus on showing how the geographical distribution of marine microorganisms, specifically microalgae, is changing – often by expanding towards higher latitudes – and the relationship this has with global warming and human activities. The problem becomes more apparent when we understand that some of these species produce toxins that can affect human health or marine ecosystems. In the terrestrial ecosystem, the COVID-19 pandemic we are currently experiencing is a good example of the rapid spread of a pathogen from a distant source to the myriad places it has come to affect. This redistribution of organisms is a common occurrence on a globalised planet. However, the problem only becomes evident with the spread of species that negatively impact human health, ecosystems, or the economy.

Returning to aquatic ecosystems, microalgae are the main primary producers in the ocean. The best-known examples are phytoplankton which, as their name suggests,[1] are a group of photosynthetic organisms with insufficient capacity for movement to exceed the physical energy of the sea and are, therefore, carried by marine currents and waves. Phytobenthic organisms can be found covering the sea floor, or more generally, between, on, or near grains of sand.[2] In recent decades, marine microalgae, whether planktonic or benthic, are experiencing a geographical species redistribution. Here, we will focus on the case of the Mediterranean, a semi-enclosed sea surrounded by densely populated land that is generally considered to be oligotrophic and with low tidal forces.

HUMAN STRESSES ON THE COASTLINE AND PROLIFERATIONS OF DINOFLAGELLATES

Seasonal phytoplankton dynamics in temperate latitudes have their optimal periods in late winter and early spring when microalgae proliferate and achieve high abundances. With agitation of the water column in winter, nutrients ascend from the deep waters to the surface layers and, coinciding with the increase in light and temperature, causes the growth

[1] *Plankton* comes from the Greek word πλαγκτός and means «wanderer».
[2] *Benthos*, βένθος, means «depth of the sea».

of microalgae communities, mainly diatoms. During the spring, different planktonic communities follow one another and consume the nutrients of the surface layers until they are almost exhausted. The sun heats the surface of the sea which forms the thermocline – a density structure that separates the superficial layers from deeper ones; this physical barrier does not allow the arrival of more nutrient supply from the bottom. Therefore, during the summer, the abundance of planktonic microalgae in superficial Mediterranean waters is low, which makes them clear and transparent. Another, more moderate, production peak occurs in autumn, when high levels of irradiance again coincides with an increase in nutrients, caused by rupture of the thermocline and mixing of the water columns.

«The human impact translates into increases in the quantity and quality of the nutrients that are dumped into rivers and the sea»

Humans exert a high pressure on the coast and, in the Mediterranean, a semi-enclosed sea surrounded by such a high population, this effect is even more noticeable. During the summer months, tourism causes the populations of some coastal towns to multiply by ten to a hundred-fold. This human impact translates into increases in the quantity and changes in the quality of the nutrients that are dumped into rivers and the sea, which cannot always be completely eliminated by sewage treatment systems. Thus, coastal waters become richer in nutrients as a result of human pressure exerted from the continental. Photosynthetic organisms (primary producers) take advantage of these nutrients of anthropic origin to grow.

Furthermore, urbanisation of the coastal zone has rendered the soil waterproof (Figure 1A); wetland areas have been virtually obliterated – paved over – from the coastal ecosystem, and what used to act in past decades as a natural filter for the nutrient-rich waters provided by the continent are now paved streets and waterways that do not filter but rather, dump everything that reaches them into coastal waters (Camp et al., 1998). Thus, they are mere conduits of enriched water which make the seawater on the immediate coast rich in nutrients, which primary producers use to grow.

Coastal foundations and rigidity also have an important effect on the sea. On the one hand, the construction of dams in riverbeds has significantly reduced the steady supply of sediments to coastal areas. In the past, these sediments were transported by coastal currents and distributed along the coast so that they provided sand to the beaches. The rhythm of nature has also been disrupted on urban beaches, with dune systems and coastal lagoons being replaced by promenades and beachfront buildings. The winter storms that carry away the sand from the beaches leave eroded beaches which cannot be restored with sand from the dune system (because none is present), or by river sediments (because these have been greatly reduced). Part of the sand washed away by the sea accumulates in breakwaters built perpendicularly to the coastline, which cut off water circulation.

Therefore, in many cases, a huge amount of sand must be moved in order to recover beaches that would have otherwise recovered on their own in the past. Thus, year after year, governments allocate part of their budgets to carry out various beach regeneration projects: costly interventions – both from an economic and an ecological point of view – which are ephemeral because they only last until the next storm arrives. Moreover, the forecast in a climate change scenario is that such storms will become more frequent and intense, such as storm Gloria reminded us at the beginning of 2020.

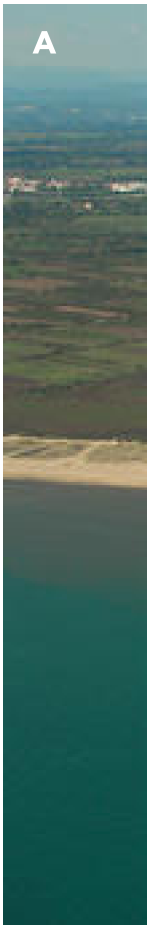

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Figure 1. Examples of coastal transformations as a product of human action: **A**) The Empuriabrava urbanisation project (Castelló d'Empúries, Girona, Spain), built on the seafront in a wetland area. Coastal wetlands have been virtually wiped out from the Mediterranean coastal ecosystem. **B**) Harbour and beach in Cambrils, Tarragona (Spain). Building harbours and breakwaters increases the volume of confined waters, an ideal habitat for dinoflagellate blooms.

«By confining coastal marine waters in ports, humans have created optimal conditions for the growth of these "red tide"-forming microalgae»

Seaports and breakwaters (Figure 1B), however, play another role. By confining waters in order to provide shelter for boats, bodies of water with high residence times that allow for the growth and accumulation of microalgae are created. Calm, shallow, nutrient-rich waters with long residence times are ideal conditions for the growth of dinoflagellates, a group of phytoplankton that produce the proliferations and colour changes popularly known as *red tides* and scientifically referred to as *harmful algal blooms*. Moreover, within the phytoplankton groups, dinoflagellates have the highest number of harmful or toxic species.

According to the mandala published by Ramon Margalef (Margalef, 1978; Margalef et al., 1979; Figure 2), the dinoflagellates that cause red tides proliferate because of the combination of high levels of nutrients with calm waters. As explained above, nutrient inputs are often related to agitation of the water column because it brings nutrients from the bottom to the surface; therefore, it is unusual to find elevated nutrient levels associated to still water; these circumstances occur naturally in bays or near

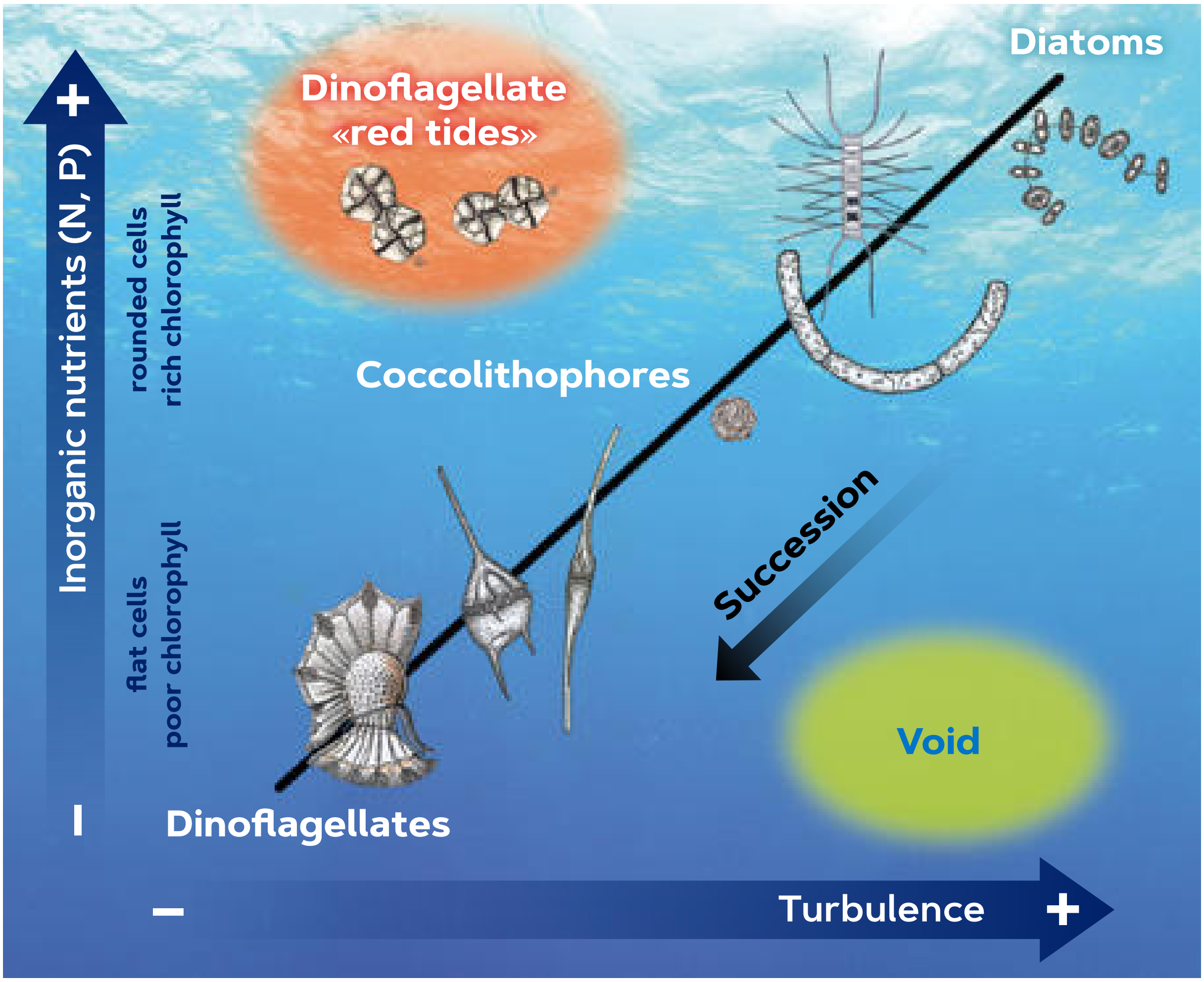

Figure 2. Ramon Margalef's mandala is a schematic representation showing how the seasonal succession of the main phytoplankton groups depends on nutrient concentration and water turbulence or agitation.

SOURCE: visual adaptation of Margalef's mandala (1978).

river mouths. By confining coastal marine waters in ports, humans have created optimal conditions for the growth of these red tide-forming microalgae. When monitoring programmes for toxic species were implemented in the Mediterranean in the 1990s, bloom-forming dinoflagellates were very well represented. This surprised experts because, according to Margalef, the Mediterranean did not have the appropriate characteristics for red tides to take place. Our hypothesis (Vila et al., 2001) was that the recreational use of coastal waters favours dinoflagellate proliferations. The construction of ports – there are currently about fifty along the Catalan coast, i.e., the equivalent of one every 8–10 km along the coastline – generates semi-enclosed water bodies with notable concentrations of nutrients, high water residence times (about twenty days), low turbulence, and low advection compared to unconfined waters, all of which favours these blooms.

Both dinoflagellate behavioural strategies (swimming, active vertical migration, and aggregation) and production of toxic compounds, are involved in reducing zooplankton predation (see Selander et al., 2015; Smayda, 1997). In addition, the concentrations of inorganic nutrients and their stoichiometric ratios indicate that areas characterised by high population densities have higher levels of ammonium and phosphates and a more limited silicate content. Therefore, they favour the growth of dinoflagellates in relation to diatoms because the latter require silicate to build their cellular covers (frustules).

Finally, ports are ideal environments in which organisms with some form of resistance (cysts or seeds) can remain confined in the sediment until new environmental conditions induce them to germinate (Anderson & Wall, 1978). Dinoflagellate blooms in harbours occur because the active growth of a small part of the germinating population is amplified by swimming and aggregation, reduction of zooplankton predation, and favourable physical factors indicated above. Therefore, a coast with many ports facilitates the colonisation and the establishment of new, non-native species. This has occurred in the case of several species from the genus *Alexandrium* (Vila et al., 2001) which can generate toxins (saxitoxins) that produce paralysing symptoms in people who eat bivalve molluscs contaminated with these organisms (Berdalet et al., 2016).

BEACHES COVERED IN MICROALGAL MATS

Some 20 or 25 years ago, blooms of benthic dinoflagellates of the genus *Ostreopsis* began to be detected during the summer months on different Mediterranean beaches. At that time, this genus was known in tropical areas to form part of the group of microorganisms (microbiota) accompanying a toxic dinoflagellate of the genus *Gambierdiscus*, which caused a tropical food poisoning known as *ciguatera* (Friedman et al., 2017). The increase in sea water temperature seems to have been the trigger for the establishment of several tropical species in the Mediterranean, which in some cases, have replaced native communities. This is known as the tropicalisation of the Mediterranean (Bianchi et al., 2018).

Ostreopsis secretes a mucous and sticky substance that keeps it softly anchored to macroalgae (Figure 3). This ability allows it to stay on beaches, close to the surface, and to proliferate relatively quickly, forming a dense carpet of microalgae and mucilage that covers the sea floor. In response to wave agitation or other factors, *Ostreopsis* detaches itself from the macro-algae and can be found swimming in the water column or floating on the surface, forming what in France is known as *water flowers*. These proliferations have been associated with massive mortalities of marine fauna that have little or no mobility (e.g., sea urchins, mussels, etc.), perhaps because of the limited oxygen availability associated with the extensive mucilaginous layer covering the seabed, or because of the production of certain toxic substances (Giussani et al., 2016; Shears & Ross, 2009).

Indeed, *Ostreopsis* produces ovatoxins, which are analogous to palytoxin. Palytoxin has been associated with lethal cases of food poisoning in the Indian Ocean in people who had consumed seafood contaminated with these compounds. These toxins enter the food chain when fauna feed on *Ostreopsis*-coated macroalgae, transmitting these toxins up to higher trophic levels, including to humans (Berdalet et al., 2017). In the Mediterranean, certain toxins associated with *Ostreopsis* have been detected in diverse marine fauna; however, food poisoning does not appear to be a problem at this time. Instead, massive proliferations of *Ostreopsis* in this area have been associated with mild respiratory irritations (rhinorrhoea, fever, general discomfort, and eye and nose irritation, etc.) in bathers and people exposed to sea spray on several beaches in Algeria, Spain, France, Italy, and Greece (Vila et al., 2016).

«Thirty years ago, *Ostreopsis* was a rare genus in the Mediterranean, detected very sporadically and in limited abundance»

A similar aerosol exposure mechanism has been confirmed as the cause of respiratory irritation symptoms during the blooms of *Karenia brevis* in the Gulf of Mexico (Fleming et al., 2011). In this case, the enormous scientific investment made by several institutions over decades of studies has provided sound knowledge that has brought about the adequate management of ecological and health risks in this area. However, in the Mediterranean, the efforts made to link these symptoms with the presence of toxins in the aerosol have provided little empirical demonstration so far (Ciminiello et al., 2014). It has been hypothesised that the irritation was not caused by the toxins themselves, but rather, by some other cell component or fragment that might have triggered some kind of reaction. It has even been speculated that the problem may have been caused by some of the microorganisms (bacteria or virus) associated with *Ostreopsis* (Bellés-Garulera et al., 2016; Casabianca et al., 2013). However, bathers with skin wounds that suffered skin irritations, were also successfully treated with topical antibiotics. All this suggests that more than one factor contributes to the various undesirable effects of *Ostreopsis* proliferations.

FINAL CONSIDERATIONS

It is evident that the Mediterranean coast has changed a lot over the last fifty years. The natural habitat of beaches and cliffs has been replaced by an artificial one comprising harbours and breakwaters, which have enclosed not only boats but also water and microalgae. Moreover, a habitat change also involves a change in species. Wetlands have been reduced to a

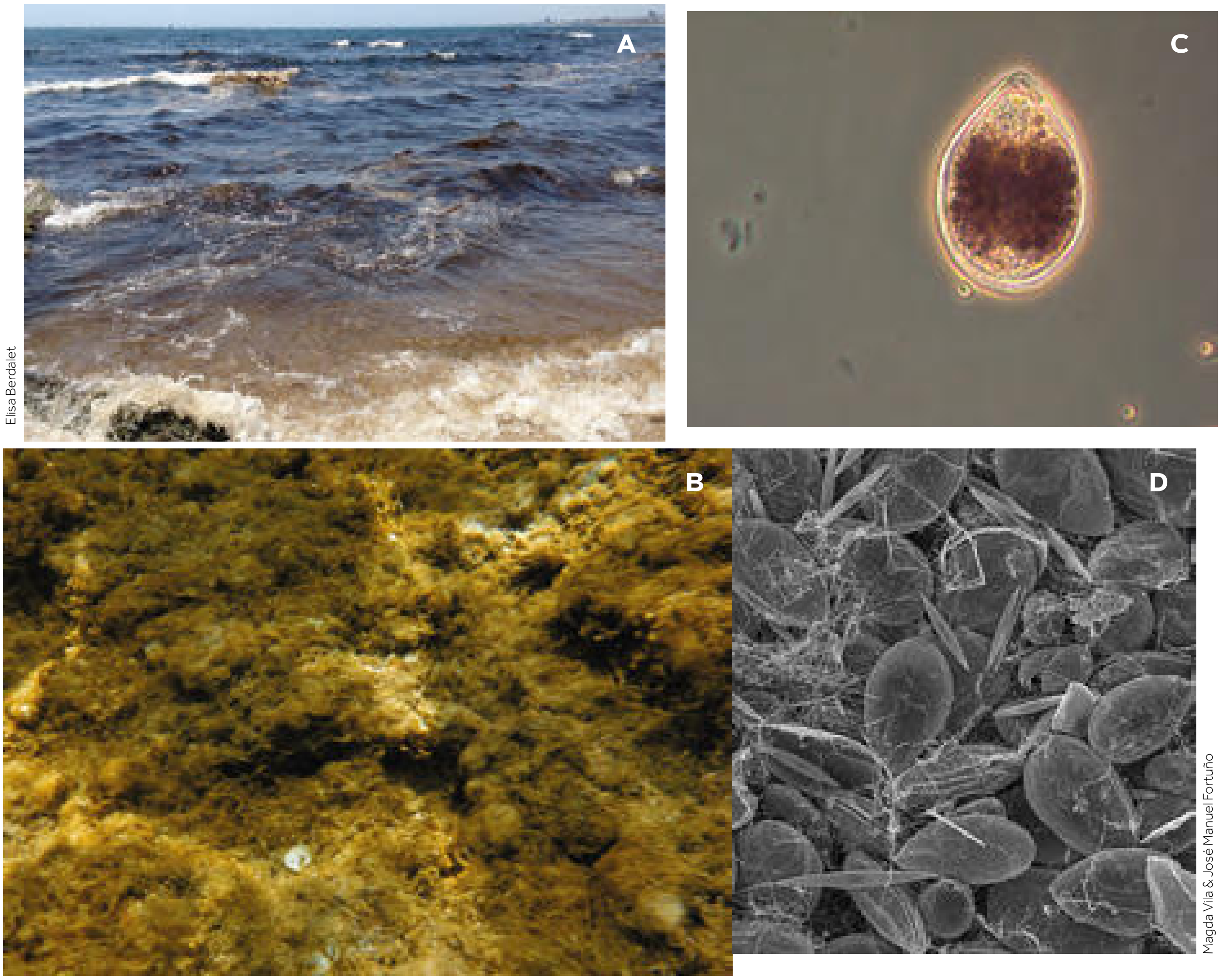

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Figure 3. Until a few years ago, it was not common to find benthic dinoflagellates of the genus *Ostreopsis* in the waters of the Mediterranean; this species is more typical in tropical areas. The increase in sea temperature appears to have caused these species to settle a new location. The pictures show: **A**) water colouration in a shallow beach covered by a proliferation of the benthic dinoflagellate *Ostreopsis;* **B**) state of a shallow seabed covered in an *Ostreopsis* bloom; **C**) *Ostreopsis* cell through an optical microscope; **D**) the appearance of a benthic proliferation dominated by *Ostreopsis* under a Scanning Electron Microscope (SEM): the network of filaments secreted by the cells can be seen.

minimum and shoreline developments have multiplied, significantly changing the flow of sediments and nutrients into the sea. Finally, with global warming, the temperature of the sea has increased, and some invasive species have arrived and settled these areas. Thus, the communities of microalgae species that existed fifty years ago have been modified or «enriched» leading, in some cases, to blooms of toxic dinoflagellates.

Planktonic proliferations of the genus *Alexandrium* are now frequent in the *Mediterranean,* and since the 1990s, they have been monitored on a weekly basis with by programmes that guarantee the safety of the food products that arrive at the fish markets and to fishmongers. Monitoring benthic microalgae is progressing more slowly because of a great lack of knowledge about Ostreopsis species until recently. Thirty years ago, this organism was a rare genus in the Mediterranean, which was detected very sporadically and in limited abundance. Now it has become a public health and environmental problem, which every year mobilises scientists and administrations, and concerns the residents of the beaches affected by these massive proliferations. By studying countries for which we currently have more information about these blooms (Mangialajo et al., 2011), it appears that what began as a massive proliferation on a particular beach during the first few years has become an expansion with multiple focal points which affects many beaches, first in Italy and France and, in the last five years, also in Catalonia. There are still many gaps in our understanding of *Ostreopsis* toxicity. However, knowledge of how it proliferates and coordination between scientists and environmental and health policy-makers has made it possible to manage the phenomenon properly and to minimise ecological and health risks.

Over the last fifty years, we have transformed our waters through direct coastal interventions such as the construction of ports and breakwaters. However, we have also constructed promenades and housing developments along the coast, with new river channelling and dams. As a result of human activity, atmospheric CO_2 and the global temperature of the planet have also increased. These direct or indirect human actions could plausibly explain why microalgae proliferation on Mediterranean coasts has increased in recent decades.

The ocean and the continent converge in a very narrow line that is nonetheless truly relevant to the health, leisure, and economy of our society. Maintaining our shores in a good ecological state can only be achieved if the activity carried out inland also upholds the standards of sustainability. In order to keep our coastline in good condition, we must rethink the world we want to live in and act accordingly. ⊙

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SAVING THE PHARMACY OF THE SEA

How does global change affect species with bioactive potential in the Mediterranean?

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Several marine species in the Mediterranean produce molecules with bioactive potential that could be used to develop new drugs (antibiotics, antifungals, antivirals, and antitumourals). Different human activities such as pollution, marine recreation, and fishing, as well as climate change, threaten and even endanger some of these species. These vulnerable species with bioactive potential must be protected, especially in marine reserves, not only because they are valuable components of marine ecosystems, but also because they are a potential source of molecules with pharmacological properties that are currently being researched for the creation of new drugs.

Keywords: global change, oceans, biodiversity, health, bioactive compounds.

INTRODUCTION

Marine organisms, which account for nearly two million species, establish highly competitive and complex relationships, often in space-constrained habitats that force them to compete very aggressively (Simmons et al., 2005). In response to this competition, many species produce chemical compounds, often called *bioactive compounds*, for several purposes: to defend themselves from predators, protect themselves from the expansion of other competing species, or capture their prey (Simmons et al., 2005). Bioactive compounds are molecules produced by a wide variety of organisms which, in the case of marine organisms, can range from bacteria, fungi, and microalgae to more complex organisms such as macroalgae, marine phanerogams, invertebrates, and vertebrates. These compounds include a wide range of molecules that are currently being researched to synthesize new products and medicines; they include anti-cancer peptides, characterised by their cytotoxic (cell damaging) and anti-tumour action (antiproliferative function, among other properties) against various tumour cell lines. These represent antibacterial, antifungal, and antiviral metabolites that can be used to make antibiotic, antifungal, and antiviral drugs, respectively. Some of them are antioxidant molecules that can protect cells from reactive oxygen species and free radicals, and others are anti-inflammatories, which can help combat some inflammatory cellular processes leading to certain diseases. They also include toxins and antitoxins, which can have various therapeutic uses, as well as complex natural products such as essential oils (Carreño & Lloret, in press; Uriz et al., 1991).

«Several species in the Mediterranean are potential sources of molecules with pharmacological properties»

Several animal and plant species in the Mediterranean Sea have bioactive potential (Uriz et al., 1991), i.e., they are a potential source of molecules with pharmacological properties that could be used to develop new antibiotic, antifungal, antiviral, or antitumour drugs. Most are sessile benthic organisms that produce molecules with bioactive potential, such as the tunicates *Ecteinascidia turbinata* and *Halocynthia papillosa*, which have anti-tumour potential; sponges such as *Spongia officinalis* and *Axinella damicornis*, with antibacterial potential; bryozoans such as *Myriapora truncata* and *Pentapora fascialis*, which also have antibacterial potential; and cnidarians such as *Pennatula aculeata* and *Actinia* *equina*, with anti-inflammatory potential. Some echinoderms such as the sea urchin *Paracentrotus lividus* and the sea cucumber *Holothuria tubulosa*, have both anti-inflammatory potential and produce bioactive compounds; molluscs such as the cuttlefish *Sepia officinalis* and squid *Loligo vulgaris*, have antibacterial potential; decapod crustaceans such as the Norway lobster (*Nephrops norvegicus*) and the Mediterranean green crab (*Carcinus mediterraneus*), have anti-tumour potential; and fish such as sardines (*Sardina pilchardus*) and the Thornback ray (*Raja clavata*), make compounds with antioxidant potential. All these animals produce a wide variety of chemical compounds that serve to defend them against their predators, competing organisms, parasites, or invasive micro-organisms (Carreño & Lloret, in press; Uriz et al., 1991).

«Despite interest in their compounds with bioactive potential, some of these species are threatened and endangered»

Despite interest in these compounds with bioactive potential for the development of future medicines, these species are also affected by climate change and human activities, and some are even threatened and endangered. Despite the critical status of some of them, studies on the impact of anthropogenic activity on their conservation status are still scarce. Thus, further studies are needed to better understand how these species cope with the impact of human activities and climate change, because if they become extinct, the possibilities these species might offer in the discovery of new medicines of marine origin will be lost too.

THE IMPACT OF GLOBAL CHANGE ON SPECIES WITH BIOACTIVE POTENTIAL

Several studies have analysed the role of species with bioactive compounds in the Mediterranean in recent years. In 2019, a review of fish and macroinvertebrate species with bioactive potential described in the scientific literature (Carreño & Lloret, in press) was carried out in the marine reserve of Cap de Creus (in northern Catalonia). They assessed vulnerability using the methodological framework established by Lloret et al. (2019), considering species that appeared on the IUCN Red List/Mediterranean Regional Assessment as threatened or in a higher threat category, and those

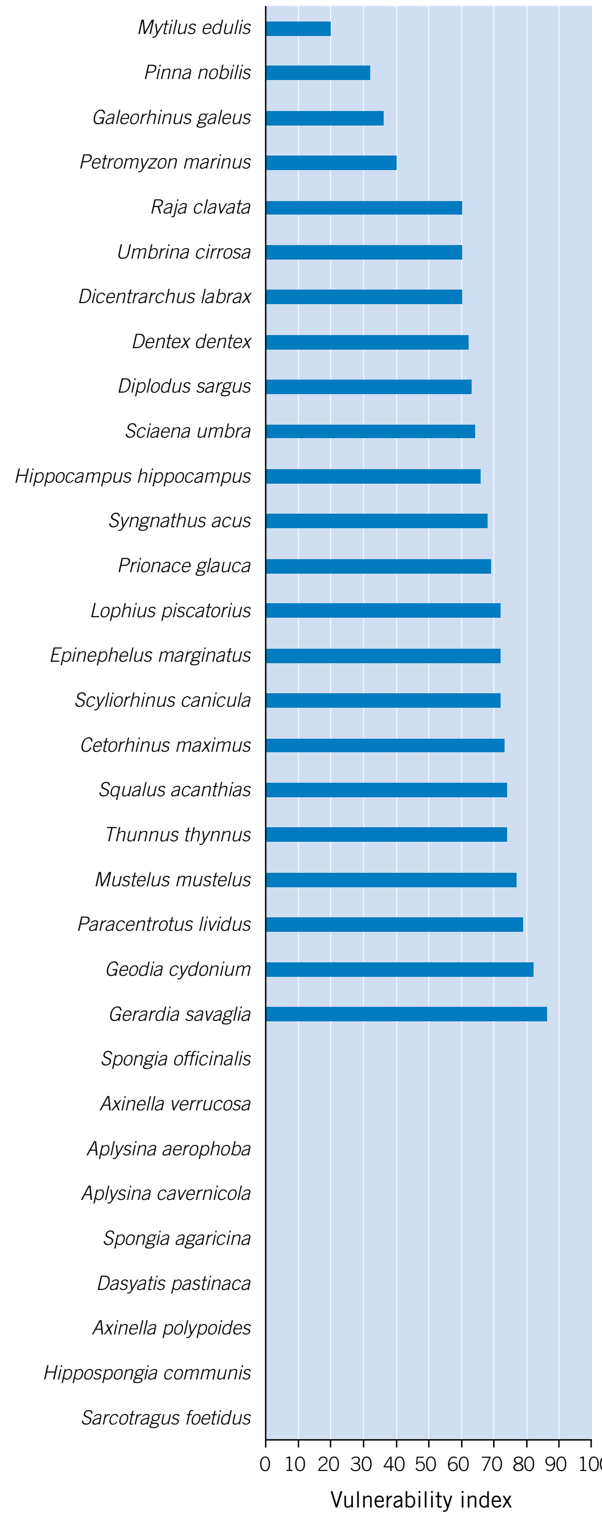
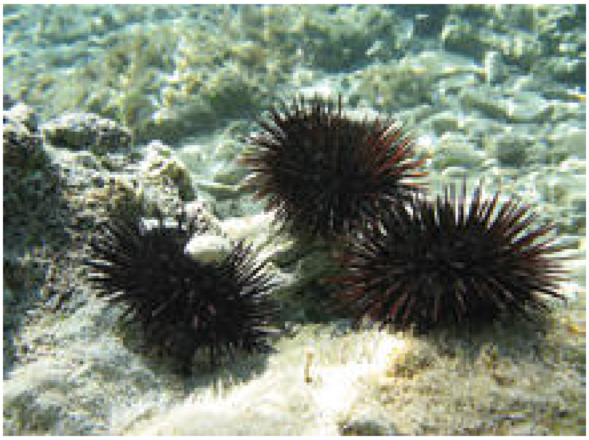


Figure 1. Mediterranean species with bioactive potential classified as vulnerable and ordered according to their vulnerability index, based on a study carried out in the Natural Park of Cap de Creus by Carreño and Lloret (in press). Blank lines correspond to species classified as vulnerable according to the criteria established in the methodology of this article, but no information on their vulnerability index was provided.

Lluís Mas Blanch



Revital Salomon

There are several animal species that produce compounds with bioactive potential in the Mediterranean Sea including molluscs such as cuttlefish (*Sepia officinalis*), with antibacterial potential (on the left), or echinoderms such as the sea urchins (*Paracentrotus lividus*), with anti-inflammatory potential (on the right).

with a vulnerability index (VI) above 60 (i.e., high to very high vulnerability, according to the index established by Cheung, Pitcher, and Pauly [2005]). Species listed in different international conventions for the protection of flora and fauna in Barcelona, Bern, or CITES, as well as in the EU Habitats Directive, were also included.

After reviewing the scientific literature[1] for information on the anthropogenic and climate change impacts on these fish and macroinvertebrate species, and reviewing studies from grey literature and research projects, we established that 32 species with bioactive potential are vulnerable and threatened by different anthropogenic factors such as pollution, marine recreation, and fishing, as well as by the action of climate change. Even though some of these species have not been sufficiently studied and so their vulnerability index is unknown, they are listed as vulnerable in the IUCN Red List or have been included in international protection conventions (Figure 1). Among these species, sponges and chondrichthyan fishes are particularly vulnerable.

«32 species with bioactive potential in the Mediterranean Sea are vulnerable and threatened by different anthropogenic factors»

Marine pollution

Marine pollution (plastics, waste, sewage, etc.) affects all marine organisms, but is particularly harmful to sessile and slow-growing organisms such as some sponges, ascidians, cnidarians, and bivalves, which include many species that produce molecules with bioactive potential. Consequently, their growth and filtration capacity are limited (Zahn et al., 1977). Waste can pollute in several ways: it can accumulate on the surface of species and inhibit their growth and cause damage such as tissue necrosis, strangulation, asphyxiation, etc. Plastics are the main source of marine pollution and rubbish, representing up to 80 % of all human-generated waste in the Mediterranean (Derraik, 2002). Plastics can also accumulate in filtering organisms or be broken down into microplastics that can be ingested by other organisms and bioaccumulate through the food chain until they reach humans (Bordbar et al., 2018). Although microplastics have been found in fish that produce molecules with antioxidant and anti-tumour potential such as mackerel (*Scomber scombrus*) or bluefin tuna (*Thunnus thynnus*), the effects on human health are still poorly understood.

The sewage that some boats still dump into the sea promotes the proliferation of toxic micro-organisms and micro-algae, which limits the exchange of oxygen in the water and leads to local anoxia. It also affects the quality of the water, because proliferation of these organisms – which take advantage of the excess organic matter in wastewater – releases large amounts of H_2S and CO_2. For example, there are areas in the Bay of Palma (Majorca, Spain) where

[1] The databases considered were ScienceDirect, PubMed, PLOS ONE, and Google Scholar. We also reviewed «grey» literature studies (reports and other work not published in indexed journals) and research projects dealing with anthropogenic impacts, especially those from the PHAROS4MPAS project (**https://pharos4mpas.interreg-med.eu/**), which compiles impacts on marine protected areas (MPAs) in the Mediterranean.

algae and marine phanerogams that may have bioactive potential – such as *Posidonia oceanica*, which contains compounds with anti-inflammatory potential – do not grow. This problem may be because of the city's wastewater discharges which might be hindering photosynthesis of *Posidonia* species. This is because, in addition to water clouding caused by particles in this wastewater, this sewage also promotes algae growth as a result of the increased presence of nutrients (Bonin-Font et al., 2018). In addition, chemicals such as industrial fats, detergents, and soaps can also cause alterations in the phytoplankton (which constitutes the basis of the food chain), obstructing the filtering capacity of organisms with bioactive potential such as certain gorgonians, corals, sponges, ascidians, and bivalves, thus causing these organisms to die (Zahn et al., 1977).


Toni Font

A


Albert Kok

C

Marine recreational activities

Motorboats and jet skis operating on shallow sandy or muddy seabeds can contribute to the generation of suspended sediments, which significantly increases water turbidity and decreases light penetration. This can cause adverse effects on algae, marine phanerogams, and other sessile animal species with bioactive potential. Suspended sediments can also directly affect certain fish that produce compounds with bioactive potential, such as the Atlantic bonito (*Sarda sarda*) and white horse mackerel (*Trachurus mediterraneus*) – both of which contain compounds with antioxidant potential – by reducing both the availability and visibility of nutrients, or by obstructing the gills of these organisms (Bruton, 1985). Turbidity not only affects water transparency, but also favours its eutrophication, which can promote the proliferation of toxic bacteria and harmful algae due to the increased presence of decomposing organic matter (Alexander & Wigart, 2013). These harmful organisms can pose a threat to both marine species and the health of humans visiting these areas.

Commercial and leisure sailing in some busy areas causes ongoing noise levels that can affect the marine fauna (including birds and mammals), leading to changes in their behaviour (Codarin et al., 2009). The noise from engines can affect certain fish that may have bioactive potential. For example, the noise from boats reduces the hearing sensitivity and ability to communicate of the brown meagre (*Sciaena umbra*) – a fish which makes compounds with anticoagulant potential (Codarin et al., 2009).

The impacts of ship anchors and chains can also damage several algae, marine phanerogams, and sessile benthic species, especially those that are slow growing and are more sensitive to pollution (Milazzo et al., 2004; Natalotto et al., 2015). From among these, Mediterranean noble pen shell (*Pinna nobilis*), which produces compounds with antioxidant potential stands out; this bivalve is currently in critical danger of extinction because of several natural and anthropogenic factors. On the one hand, its survival is threatened by the anchoring of recreational boats (Hendriks et al., 2013) and marine pollution (Natalotto

Some plant species in the Mediterranean are potential sources of molecules with pharmacological properties that could be used to research new drugs. Most are sessile, benthic organisms like the ones in the pictures: **A**) the cnidarian *Actinia equina*, with anti-inflammatory potential; **B**) the sponge *Axinella damicornis*, with antibacterial potential; or **C**) the tunicate *Halocynthia papillosa*, with anti-tumoural potential.

et al., 2015), and on the other hand, because of high mortality caused by a recent disease attributed to the endoparasite protozoan *Haplosporidium pinnae* (Cabanellas-Reboredo et al., 2019).

However, sessile organisms with bioactive potential are not only affected by boats; other leisure activities that can involve contact with the benthos, such as underwater fishing or diving, can also sometimes impact these organisms. This is the case of the bryozoan *Pentapora fascialis* (with antibacterial potential), which is damaged by impacts from the flippers of inexperienced divers and underwater fishermen (Casoli et al., 2017).

«Marine pollution is particularly harmful to sessile and slow-growing organisms»

Fishing

Some professional fishing methods, such as trawling, dramatically affect marine habitats and species (Pipitone et al., 2000). Many types of fish are not targeted by fishing activity because they have little or no commercial value) and so these are usually part of discards. Nonetheless, several of these have bioactive potential, including the greater pipefish *Syngnathus acus* and greater weever *Trachinus draco*, with cytotoxic and anti-tumour potential, respectively. Also of note are several species which produce molecules with anti-tumour potential such as tuna, smooth-hound (*Mustelus mustelus*), basking shark (*Cetorhinus maximus*), and common stingray (*Dasyatis pastinaca*) – all of which are on the IUCN Red List and are included in several international conventions for the protection of fauna such as CITES (Barcelona) and Bern.

On the other hand, fish populations with bioactive potential are threatened not only by the action of large-scale commercial fishing, but sometimes also by small-scale and recreational fishing (Lloret et al., 2019), as is the case of the dusky grouper (*Epinephelus marginatus*), gilt-head bream (*Sparus aurata*), and common dentex (*Dentex dentex*): species that all produce molecules with antibacterial potential (Lloret et al., 2019). The skin of blue sharks (*Prionace glauca*) has antioxidant properties, but it is also one of the most commercially exploited shark species in surface longlining and by some recreational fishermen. The blue shark is listed in the IUCN Red List as globally threatened, but its population is especially declining in the Mediterranean where it is currently classified as «critically endangered». Although recreational fishermen in Spain are not allowed to fish for it, they are also not required to report their catch. Therefore, the overall impact of recreational fishing on sharks is difficult to quantify (Lloret et al., 2019).

Finally, the operation of fishing gear causes a lot of damage to sessile species (gorgonians, for example) through abrasion, strangulation, etc. Vagile species are also affected by «ghost» fishing, caused by fishing gear lost at the bottom of the sea that continues to catch fish (Lloret et al., 2014) and thus, constitutes a threat to these species with bioactive potential.

Warmer waters

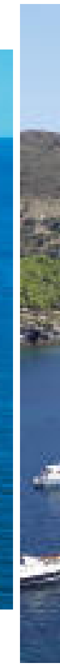
It is a well-known fact that the temperature of seawater in the Mediterranean has increased as a result of climate change, and that this warming is negatively affecting the growth and survival of sessile species with bioactive potential such as the gorgonian *Paramuricea clavata* and red coral (*Corallium rubrum*) (Verdura et al., 2019).

Warming of marine waters can also lead to massive species mortality because of the proliferation of opportunistic thermophilic pathogens (Trainer & Hardy, 2015). Algae proliferations are increasingly common, and these can both release toxic substances that directly induce mortality among fish, crustaceans, and mollusc species, and cause anoxia in shallow seas such as the Mar Menor, thereby causing significant ecological impacts (Erena et al., 2019). The latter example is not only caused by warming of the ocean, but also by the sudden supply of nutrients from rivers during periods of intense rain, which favours the proliferation of microorganisms in these shallow waters.

Finally, the increase in sea temperature can also displace species with bioactive potential into colder waters, as in the case of sardines (*Sardina pilchardus*) and mackerel, while encouraging the appearance of thermophilic species, which can sometimes be invasive (Katsanevakis et al., 2014) or even dangerous to human health. A good example is the silver-cheeked pufferfish *Lagocephalus sceleratus*, which is expanding into the Mediterranean (especially on the eastern shores) from the Red Sea through the Suez Canal, aided by increased sea water temperatures. Besides being invasive and disrupting the food web in the new areas in which it has established itself (Coro et al., 2018), this species is poisonous and produces a potentially fatal toxin, tetrodotoxin (TTX), which causes paralysis and death to those who ingest it (Nieto et al., 2012). Therefore, the Suez Canal represents an added problem to the already complicated management of water warming because it is the source of a constant influx of new species (an estimated 700 and 1,000 invasive species) into the Mediterranean. In addition to pufferfish, other invasive and potentially dangerous

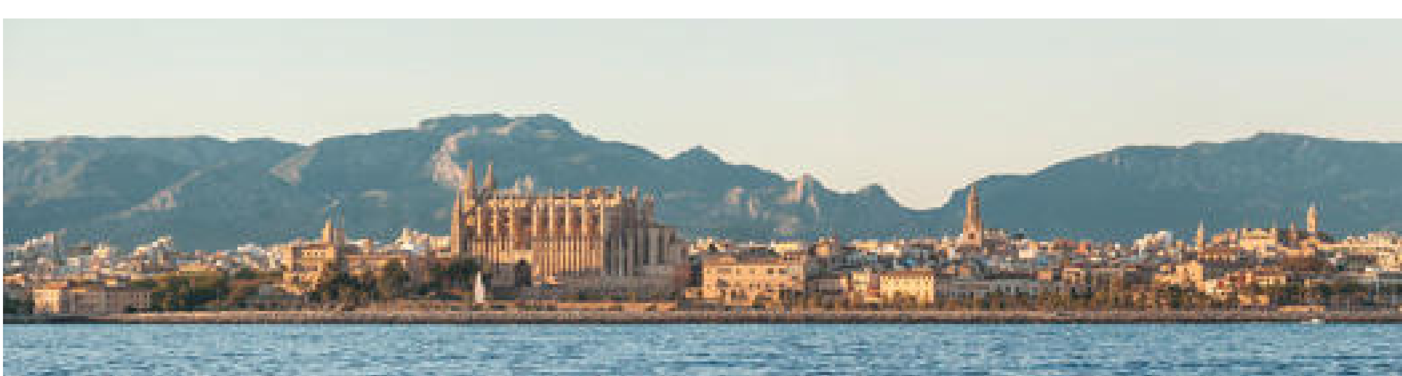
Marie-Schneider-en-Pixabay

Commercial and leisure sailing in some busy areas causes ongoing noise levels that can affect the marine fauna, leading to changes in behaviour. It also affects species that may have bioactive potential, such as the brown meagre (*Sciaena umbra*), which has compounds with anticoagulant potential and suffers reduced hearing and communication sensitivity as a result of noise from ships.



«Not only boats affect sessile organisms with bioactive potential; other activities such as fishing, or diving can also impact them»

Pollution has negative effects on the growth and development of marine species. There are areas in the Bay of Palma (Majorca, Spain) where algae and marine phanerogams that may have bioactive potential do not grow. Experts suspect that this is caused by the city's wastewater discharges, which hinder *Posidonia* photosynthesis and promote the proliferation of other algae as a result of the new nutrients being delivered into the area.



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The impacts of ship anchors and chains can also damage many algae, marine phanerogams, and sessile benthic organisms, especially those that are slow growing and which are more sensitive to pollution.

organisms that have been introduced into the ecosystem via the Suez Canal are red lionfish (*Pterois volitans*) and several species of toxic jellyfish such as *Rhopilema nomadica*.

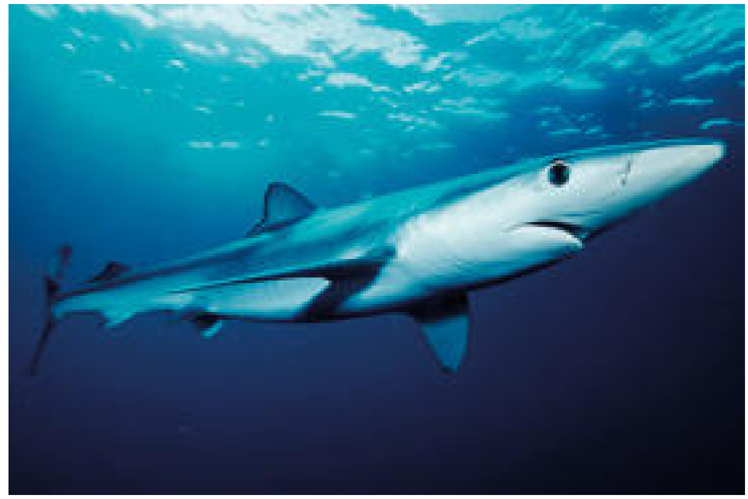
In contrast, warming waters also threaten the survival of native species which produce bioactive compounds that may be useful against emerging and highly topical diseases. For example, a drug called Aplidin has been derived from the sea squirt *Aplidium albicans* which is currently being used to combat some types of myeloma (cancer) and is also being studied as a possible treatment for COVID-19 (PharmaMar, 2020). Thus, there is an urgent need to protect species with bioactive potential that can provide effective medicines to combat new diseases.

While the increase in sea water temperature appears to have been detrimental to these species with bioactive potential, this warming could also potentially provide opportunities for thermophilic species that can benefit from the increase in sea temperature and may also produce compounds with bioactive potential. Examples include the round sardinella (*Sardinella aurita*), a species that has antioxidant potential, and cuttlefish (*Sepia pharaonis*), which have a cytotoxic potential. Moreover, tetrodotoxin extracted from the invasive pufferfish *Lagocephalus sceleratus* is now being used in the synthesis of new analgesic medicines to alleviate chronic pain (Nieto et al., 2012) and venom from (*Scorpaena plumieri* (Campos et al., 2016) contains both inflammatory and cytotoxic bioactive compounds. The heating of the waters also favours the proliferation of algae and microorganisms that can produce toxins with bioactive potential, including the dinoflagellate *Karenia brevis* in the Gulf of Mexico, which is currently being examined because it may provide a new medicine to treat cystic fibrosis (Potera, 2007). Warmer waters may also be contributing to an increase in jellyfish populations (Boero et al., 2016), among which some, like *Rhizostoma pulmo* and *Pelagia noctiluca*, have cytotoxic bioactive potentials.

DISCUSSION AND CONCLUSIONS

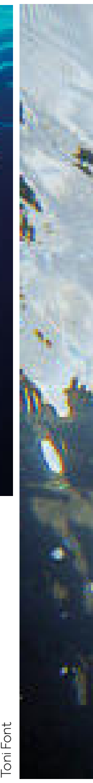
Although many species with bioactive potential in the Mediterranean are vulnerable to global change and are listed in international conventions for the protection of species, they are not legally protected. A recent study (Carreño & Lloret, in press) indicates that around 20 % of the fish and marine macroinvertebrate species documented in Cap de Creus have bioactive

potential, with 20 % of them also having been classified as vulnerable. New management measures are needed to protect vulnerable species with bioactive potential, including monitoring their stocks, establishing new regulations, and creating new marine protected areas. It will also be important to carry out outreach activities aimed at fishermen and marine recreation businesses (diving, sailing, etc.), as well as with the general public, to raise awareness of the importance of protecting these spaces. Species with bioactive potential must be protected not only because they are valuable components of marine ecosystems, but also because they are a potential source of molecules with pharmacological properties that could be used to research new drugs for treating diseases such as cancer. In this sense, we recommend that the policy-makers responsible for marine ecosystems consider the bioactive potential of vulnerable species and consider new measures to protect them, particularly in marine reserves, which constitute a veritable «pharmacy of the sea».



Mark Conlin/MFNS

The skin of blue sharks (*Prionace glauca*) has antioxidant properties. This species is listed in the IUCN Red List as globally threatened, but in the Mediterranean its population is declining and it is currently classified as «critically endangered». Although recreational fishermen in Spain are not allowed to fish for it, they are also not required to report their catch.



Toni Font

«Several species with bioactive potential are vulnerable to global change»

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Laszlo Ilyes

An increase in sea temperature can provide opportunities to thermophilic species that may also produce compounds with bioactive potential. This is the case of jellyfish like *Rhizostoma pulmo*, on the left, with cytotoxic potential, or *Scorpaena plumieri*, on the right, with inflammatory and cytotoxic bioactive compounds.

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